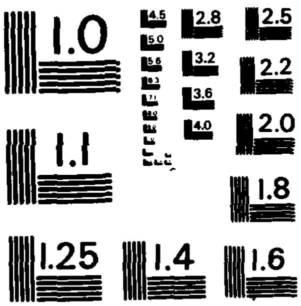
AD-A133 957 SYMPOSIUM ON MOLECULAR SPECTROSCOPY (38TH) HELD AT OHIO 1/2
STATE UNIVERSITY COLUMBUS OHIO ON JUNE 13-17 1983(U)
OHIO STATE UNIV COLUMBUS 1983

UNCLASSIFIED F/G 7/4 NL



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

PLANS FOR THE 39TH MOLECULAR SPECTROSCOPY SYMPOSIUM
THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO
JUNE 11-15, 1984

The usual first mailing will be sent about the end of 1983 updating the list of Invited Speakers given below:

1. Dr. Robert W. Field, Massachusetts Institute of Technology,
   Dr. Takeshi Oka, University of Chicago,
   Dr. Richard J. Saykally, University of California, Berkeley.

2. A special "SEMINAR ON HYDROGEN" (gas phase as well as solid state) is being organized.

   Dr. I. F. Silvera, Harvard University and Dr. J. Van Kranendonk, University of Toronto, have accepted to speak on different aspects of hydrogen.

   Dr. R. H. Tipping of the University of Alabama, who is currently associated with the Air Force Geophysical Laboratory is coordinating some of the arrangements for this seminar.

3. Attempts are being made to arrange a "SPECIAL SEMINAR" on the calculation of diatomic potential curves, dissociation energies and spin-orbit effects, in conjunction with the American Conference on Theoretical Chemistry which will start at the end of the week of the 39th Molecular Spectroscopy Symposium here on June 15, 1984.

   Professor R. H. Pitzer of the Ohio State University is in charge of the arrangements for this special seminar at the Ohio State University.

4. Coblentz Society will continue their participation.

5. Deadline for receipt of Contributed Papers: March 1, 1984.

   Please follow the format reproduced on the back of this page. It is the same as in the previous years. We realize that another format may look satisfactory but it will not contribute to our being able to maintain some uniformity. We feel that it will look nice all the way around if there is complete compliance on this matter.

Thank you for your cooperation.

START HERE THIS DIMENSION MUST BE PRESERVED FOR EVERY ABSTRACT

8 in. (~20 cm)

THIS DIMENSION SHOULD BE 6 in. (~15 cm) or less

HIGH RESOLUTION FOURIER SPECTROSCOPY OF THE Ar^+ LASER 5145 Å EXCITED I_2 FLUORESCENCE SPECTRUM

R. BACIS, S. CHURASSY, R. W. FIELD, J. B. KOFFEND, AND J. VERGES

This preliminary work demonstrates the feasibility of obtaining a high resolution spectrum of cw laser excited fluorescence using a Fourier spectrometer.

Using 1.3W of 5145 Å multimode power from an Ar^+ laser, fluorescence is excited mainly via the P(13) and R(15) (43,0) lines. Nearly all of the ... fluorescence lines [P(13), P(17), R(11), R(15)] originating from v' = 43 are observed ... 85. Their recorded full width at half maximum in the 7000-8000 cm^{-1} region ...

Rotational relaxation ($\Delta J'$ - ... rous odd-J" satellite lines. The usual parameters are obtain... rotation-vibration levels of I_2 $X^1\Sigma^+$ through v" = 85.

The vibrational line intensi... the alternation pattern predicted by the Franck-Condon factors of Tellingh... ...ne agreement between measured and calculated intensities is only qualitative for ...gh v" values. This has important implications with respect to the I_2 laser gain measurements discussed in the following talk.

This sample abstract gives the required format

Will be copied photographically

[1] J. Tellinghuisen, J. Quant. Spect. Rad. Transf. 19, 149 (1978).

Address of Bacis and Churassy: Laboratoire de Spectrométrie Ionique et Moléculaire 43, bd du 11 Novembre 1918, 69621 - Villeurbanne, France.
Address of Field and Koffend: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139.
Address of Verges: Laboratoire Aimé Cotton - C.N.R.S. II, Bâtiment 505, 91405 - Orsay, France.

Time required: 15, 10 or 5 min.

Session in which paper is recommended for presentation:_____

Chemical formulas & sketches of molecular structures for larger molecules:

PLEASE NOTE:

1. Use good quality bond paper and an electric typewriter when preparing your Abstract. In the space for title and abstract you may include tables, equations and line drawings.
2. Send an original and one copy.
3. Please use a larger envelope for mailing. Do not fold.
4. *Underline the name of the person who will be presenting the paper.*
5. Include only the TITLE, AUTHORS' NAMES, and TEXT in the abstract. The author's affiliation should be given separately, as shown in the example.
6. Supply chemical formulas and rough sketches of structures of the larger molecules. This information is useful in arranging sessions.

General categories of sessions:

(1) Electronic (large molecules)	(6) Laser spectra	(11) Raman spectra
(2) Electronic (small molecules)	(7) Liquid state	(12) Solid state (electronic)
(3) Electronic (theory)	(8) Matrix spectra	(13) Solid state (infrared)
(4) Energy transfer	(9) Microwave	(14) Techniques
(5) High resolution IR & THEORY	(10) Molecular beam	(15) Vibrational analysis

MONDAY, JUNE 13, 1983 -- 9:30 A.M.

Auditorium, Independence Hall

Chairman: S. LESLIE BLATT, Chairman, Department of Physics, The Ohio State University, Columbus, Ohio.

Plenary Session

MA. THE SPECTROSCOPY OF ORGANIC DIMERS........................40 min.

DONALD H. LEVY, The James Franck Institute, The University of Chicago, Chicago, Illinois, 60637.

MA2. HIGH RESOLUTION INFRARED SPECTROSCOPY--ARRIVED IN BOMBAY IN 1980--SUBSEQUENT DEVELOPMENTS (Aspects of Indo-U.S. Program on Science & Technology)............40 min.

ROMOLA D'CUNHA, Spectroscopy Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India, and Department of Physics, The Ohio State University, Columbus, Ohio, 43210.

MA3. RECENT STUDIES OF NUCLEAR HYPERFINE EFFECTS IN THE INFRARED SPECTRA OF SPHERICAL-TOP MOLECULES..............40 min.

JACQUES BORDÉ, Laboratoire de Physique des Lasers, Universite Paris-Nord, Laboratoire Associe au CNRS No. 282, 93430 Villetaneuse, Paris, France.

PLEASE NOTE:

ALL PAPERS IN THE Σ AND Π SESSIONS HAVE BEEN SCHEDULED FOR PRESENTATION. THE LISTS OF THESE LATE PAPERS APPEAR ON PAGES 37-38 FOR Σ AND 39-40 FOR Π. THE ABSTRACTS FOR THESE PAPERS HAVE BEEN INCLUDED IN THE SESSIONS IN WHICH THE PAPERS ARE ACTUALLY BEING PRESENTED. PLEASE NOTE THAT A NEW SESSION FD HAS BEEN ADDED SINCE THE PROGRAM WAS FIRST PREPARED IN MARCH. THE SCHEDULE OF PAPERS IN THIS SESSION FD APPEARS ON PAGE 40. THE LOGISTICS INVOLVED IN THE PREPARATION OF THE PROGRAM AND ABSTRACTS NECESSITATED THIS PROCEDURE. IF THERE IS ANY CONFUSION, PLEASE SPEAK TO ME.

THANK YOU,

K. Narahari Rao.

MONDAY, JUNE 13, 1983 -- 1:30 P.M.

Room 1153, Physics Laboratory

Chairman: LARRY PUGH, Rocketdyne, Canoga Park, California.

ME1. MEASUREMENTS OF VARIOUS ISOTOPIC RATIOS AT THE 0.1 PERCENT PRECISION LEVEL WITH A COMPUTER CONTROLLED DIODE LASER SPECTROMETER SYSTEM.................. 15 min.(1:30)

R. L. SAMS and J. R. DEVOE, National Bureau of Standards, Center for Analytical Chemistry, Laser Analytical Chemistry Group, Washington D.C., 20234.

ME2. LINE INTENSITY MEASUREMENTS OF ISOTOPIC, HOT BAND, AND HOT HOT BAND TRANSITIONS IN THE ν_2 REGION OF CARBON DIOXIDE.............................. 10 min.(1:47)

J. O'CONNELL, A. W. MANTZ, Laser Analytics, Inc., 25 Wiggins Avenue, Bedford, Massachusetts, 01730; W. O. GALLERY, and S. A. CLOUGH, Air Force Geophysics Laboratory/OPI, Hanscom Air Force Base, Massachusetts, 01731.

ME3. WING CORRECTIONS TO MEASURED HALF-WIDTHS.................................. 15 min.(1:59)

BERNARD FRIDOVICH, NOAA/NESDIS, FOB #4, E/RA21, Washington, D.C., 20233.

ME4. STRENGTHS, HALF-WIDTHS, AND TEMPERATURE DEPENDENCE OF HALF-WIDTH, FOR R BRANCH SPECTRAL LINES IN THE ν_3 AND $(\nu_2+\nu_3)-\nu_2$ BANDS OF CO_2 NEAR 4.3 μm, MEASURED WITH A DIODE LASER.. 10 min.(2:16)

V. MALATHY DEVI, BERNARD FRIDOVICH, D. J. JONES, and D.G.S. SNYDER, NOAA/NESDIS, FOB #4, E/RA21, Washington, D.C., 20233.

ME5. FOREIGN GAS BROADENED WIDTHS OF CO_2 AT 9.4 AND 10.4 μm...................... 10 min.(2:28)

M. HOKE, B. HAWKINS, and J. SHAW, Department of Physics, The Ohio State University, Columbus, Ohio, 43210.

ME6. LINE PARAMETERS FOR THE 5-μm BANDS OF CARBON DIOXIDE....................... 10 min.(2:40)

C. P. RINSLAND, D. C. BENNER, Department of Physics, College of William and Mary, Williamsburg, Virginia, 23185; D. J. RICHARDSON, Systems and Applied Sciences Corporation, Hampton, Virginia, 23665; and M.A.H. SMITH, NASA Langley Research Center, Mail Stop 401A, Hampton, Virginia, 23665.

ME7. MOLECULAR CONSTANTS OF $^{12}C^{16}O_2$ BANDS IN 1900 $cm^{-1}\sim$ 2150 cm^{-1}................ 10 min.(2:52)

HAJIME SAKAI, Astronomy Research Facility, University of Massachusetts, Amherst, Massachusetts, 01003.

Intermission

ME8. $^{12}C^{16}O^{18}O$: HIGH RESOLUTION EMISSION SPECTRA BY FOURIER TRANSFORM SPECTROSCOPY (FROM 2000 TO 2400 CM^{-1})...................................... 15 min.(3:15)

D. BAILLY, G. GUELACHVILI, and C. ROSSETTI, Laboratoire d'Infrarouge, Université de Paris-Sud, 91405 Orsay, France.

ME9. ANALYSIS OF $\Delta v_3 = 1$ BANDS AT 800K $^{13}C^{16}O_2$ AND $^{13}C^{16}O^{18}O$........................ 10 min.(3:32)

MARK P. ESPLIN, Stewart Radiance Laboratory, Utah State University, Bedford, Massachusetts, 01730; and LAURENCE S. ROTHMAN, Optical Physics Division, U.S. Air Force Geophysics Laboratory, Hanscom Air Force Base, Massachusetts, 01731.

ME10. TUNABLE DIODE LASER MEASUREMENTS OF INTENSITIES AND SELF-BROADENED WIDTHS OF THE 00^01-10^00 BAND OF N_2O.. 10 min.(3:44)

C. A. DEJOSEPH, JR. and D. R. POND, AFWAL/POOC-3, Wright-Patterson Air Force Base, Ohio, 45433.

ME11. INTENSITIES AND COLLISIONAL LINEWIDTHS OF N_2O FROM FOURIER TRANSFORM SPECTRA... 15 min.(3:56)

N. LACOME, A. LEVY, and G. GUELACHVILI, Laboratoire d'Infrarouge, Université de Paris-Sud, 91405 Orsay, France.

ME12. TEMPERATURE DEPENDENCE OF THE O_2-BROADENED LINE WIDTHS OF N_2O.............. 10 min.(4:13)

R. L. HAWKINS and J. H. SHAW, Department of Physics, The Ohio State University, Columbus, Ohio, 43210.

ME13. THEORETICAL DETERMINATION OF N_2-BROADENED HALFWIDTHS OF OZONE..............10 min.(4:25)

R. R. GAMACHE, The Center for Atmospheric Research, University of Lowell Research Foundation, Lowell, Massachusetts, 01854; R. W. DAVIES, GTE/Sylvania, 40 Sylvan Road, Waltham, Massachusetts, 02154; and L. S. ROTHMAN, Optics Division, Air Force Geophysics Laboratory, Hanscom Air Force Base, Massachusetts, 01731.

ME14. DIODE LASER LABORATORY SPECTROSCOPY SUPPORTING THE 12μm HETERODYNE DETECTION OF C_2H_6 ON JUPITER..15 min.(4:37)

D. E. JENNINGS, Laboratory for Extraterrestrial Physics, Infrared and Radio Astronomy Branch, NASA-Goddard Space Flight Center, Greenbelt, Maryland, 20771.

ME15. Σ7 will be presented here(A. S-C. CHEUNG)..................................10 min.(4:54)

MONDAY, JUNE 13, 1983 -- 1:30 P.M.

Room 1009, Physics Laboratory

Chairman: R. D. KNIGHT, Department of Physics, The Ohio State University, Columbus, Ohio.

MF1. LINE ASSIGNMENTS IN THE H-F STRETCHING FUNDAMENTALS OF THE HF DIMER.........15 min.(1:30)

W. J. LAFFERTY and A. S. PINE, Molecular Spectroscopy Division, National Bureau of Standards, Washington D.C., 20234.

MF2. MILLIMETER WAVE INVESTIGATION OF THE HF DIMER..............................15 min.(1:47)

R. D. SUENRAM, F. J. LOVAS, and W. J. LAFFERTY, Molecular Spectroscopy Division, National Bureau of Standards, Washington D.C., 20234.

MF3. MILLIMETER WAVELENGTH STUDY OF THE HF-H_2CO SYSTEM..........................15 min.(2:04)

F. J. LOVAS and R. D. SUENRAM, Molecular Spectroscopy Division, National Bureau of Standards, Washington D.C., 20234.

MF4. MILLIMETER AND SUBMILLIMETER SPECTROSCOPY OF MOLECULAR IONS IN A NEW MAGNETICALLY ENHANCED SOURCE..15 min.(2:21)

GRANT M. PLUMMER, Department of Physics, Duke University, Durham, North Carolina, 27706; GEOFFREY A. BLAKE, Department of Chemistry, California Institute of Technology, Pasadena, California, 91125; WAYNE C. BOWMAN, Bell Laboratories, Whippany, New Jersey, 07981; ERIC HERBST and FRANK C. DE LUCIA, Department of Physics, Duke University, Durham, North Carolina, 27706.

MF5. MICROWAVE SPECTROSCOPY OF WATER BETWEEN 500 GHz AND 1000 GHz...............15 min.(2:38)

JAMES K. MESSER, Department of Physics, Duke University, Durham, North Carolina, 27706; PAUL HELMINGER, Department of Physics, University of South Alabama, Mobile, Alabama, 36688; and FRANK C. DE LUCIA, Department of Physics, Duke University, Durham, North Carolina, 27706.

Intermission

MF6. EXCITATION MECHANISMS IN THE HCN FIR LASER.................................15 min.(3:10)

DAVID D. SKATRUD, Department of Physics, Duke University, Durham, North Carolina, 27706; GEOFFREY A. BLAKE, Department of Chemistry, California Institute of Technology, Pasadena, California, 91125; K.V.L.N. SASTRY, Department of Physics, University of New Brunswick, Fredericton, New Brunswick, E3B 5A3, Canada; and FRANK C. DE LUCIA, Department of Physics, Duke University, Durham, North Carolina, 27706.

MF7. ENERGY TRANSFER MECHANISMS AND TWO PHOTON EFFECTS IN $^{13}CH_3F$................15 min.(3:27)

WILLIAM H. MATTESON, DAVID D. SKATRUD, and FRANK C. DE LUCIA, Department of Physics, Duke University, Durham, North Carolina, 27706.

MF8. TONE-BURST MODULATION COLOR CENTER LASER SPECTROSCOPY......................10 min.(3:44)

CHRISTOPHER S. GUDEMAN, MARIANNE H. BEGEMANN, JÜRGEN PFAFF, and RICHARD J. SAYKALLY, Department of Chemistry, University of California, Berkeley, California, 94720.

MF9. VELOCITY MODULATED LASER ABSORPTION SPECTROSCOPY OF MOLECULAR IONS..........15 min.(3:54)

CHRISTOPHER S. GUDEMAN, MARIANNE H. BEGEMANN, and RICHARD J. SAYKALLY, Department of Chemistry, University of California, Berkeley, California, 94720.

MF10. MEASUREMENT OF THE ν_1 BAND OF HCO^+.......................................15 min.(4:09)

CHRISTOPHER S. GUDEMAN, MARIANNE H. BEGEMANN, JÜRGEN PFAFF, and RICHARD J. SAYKALLY, Department of Chemistry, University of California, Berkeley, California, 94720.

MF11. MEASUREMENT OF THE ν_1 BAND OF HNN^+.......................................15 min.(4:26)

MARIANNE H. BEGEMANN, CHRISTOPHER S. GUDEMAN, JÜRGEN PFAFF, and RICHARD J. SAYKALLY, Department of Chemistry, University of California, Berkeley, California, 94720.

MF12. ULTRAVIOLET LASER INDUCED FLUORESCENCE SPECTROSCOPY OF MOLECULAR IONS IN A RADIOFREQUENCY ION TRAP...15 min.(4:43)

CECILIA MARTNER, JÜRGEN PFAFF, NEIL ROSENBAUM, and RICHARD J. SAYKALLY, Department of Chemistry, University of California, Berkeley, California, 94720.

MF13. Σ10 *will be presented here*(NATHAN N. HAESE)...............................10 min(5:00)

MONDAY, JUNE 13, 1983 -- 1:30 P.M.

Room 1005, Physics Laboratory

Chairman: W. R. MOOMAW, Department of Chemistry, Williams College, Williamstown, Massachusetts.

MG1. TWO LASER FRAGMENTATION STUDY OF BUTADIENE .... 15 min. (1:30)

A. M. WOODWARD, S. D. COLSON, W. A. CHUPKA, and M. S. SEAVER, Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut, 06511.

MG2. PREPARATION AND PHOTODISSOCIATION OF CH_3I^+ BY MULTIPHOTON PROCESSES .... 15 min. (1:47)

A. M. WOODWARD, S. D. COLSON, W. A. CHUPKA, and M. S. SEAVER, Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut, 06511.

MG3. RESONANT MULTIPHOTON IONIZATION AND ELECTRON IMPACT SPECTROSCOPIC INVESTIGATIONS OF DIENES .... 15 min. (2:04)

A. SABLJIĆ, R. MCDIARMID, National Institutes of Health, Bethesda, Maryland, 20205; and J. P. DOERING, Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland, 21218.

MG4. ELECTRONIC SPECTRA OF CONCENTRATED SOLUTIONS .... 5 min. (2:21)

LEIGH B. CLARK, Department of Chemistry, University of California-San Diego, La Jolla, California, 92093.

MG5. POLARIZED ELECTRONIC SPECTRA OF PYRIMIDINES .... 10 min. (2:28)

JOEL NOVROS, The Johns Hopkins University, Baltimore, Maryland, 21218; FRANK ZALOUDEK, The Charles University, Prague, Czechoslovakia; and LEIGH B. CLARK, Department of Chemistry, University of California-San Diego, La Jolla, California, 92093.

MG6. TIME-RESOLVED FLUORESCENCE DEPOLARIZATION IN THE DECAY OF INTERMEDIATE CASE MOLECULES. ZERO-FIELD LEVEL CROSSING OF THE MOLECULAR EIGENSTATES OF $^1B_{3u}$ PYRAZINE .... 15 min. (2:40)

Y. MATSUMOTO, L. H. SPANGLER, and D. W. PRATT, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, 15260.

Intermission

MG7. ON THE ORIGIN OF THE ROTATIONAL STATE DEPENDENCE OF THE DECAY OF $^1B_{3u}$ PYRAZINE. ANGULAR MOMENTUM SELECTION RULES IN INTERSYSTEM CROSSING .... 15 min. (3:10)

Y. MATSUMOTO, L. H. SPANGLER, and D. W. PRATT, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, 15260.

MG8. MAGNETIC FIELD EFFECTS ON THE DECAY OF $^1B_{3u}$ PYRAZINE IN A SUPERSONIC JET.... 15 min. (3:27)

L. H. SPANGLER, Y. MATSUMOTO, and D. W. PRATT, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, 15260.

MG9. LASER INDUCED FLUORESCENCE EXCITATION SPECTRA OF 1-FLUORO, 1-CHLORO, AND 1-BROMONAPHTHALENE IN A SUPERSONIC JET .... 15 min. (3:44)

M. V. RAMAKRISHNA and D. W. PRATT, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, 15260.

MG10. OPTICALLY DETECTED MAGNETIC RESONANCE STUDIES OF TRIPLET CYCLOPENTANONE AND SOME OF ITS ISOTOPICALLY LABELED DERIVATIVES .... 15 min. (4:01)

W. BRYAN LYNCH and D. W. PRATT, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, 15260.

MG11. ELECTRONIC EXCITED STATE PROPERTIES OF SEVERAL SMALL RING COMPOUNDS .... 15 min. (4:18)

D. D. ALTENLOH, L. LIN, L. ASHWORTH, and B. R. RUSSELL, Department of Chemistry, North Texas State University, Denton, Texas, 76203.

MG12. TWO-PHOTON EXCITATION SPECTRUM OF PERYLENE .... 15 min. (4:35)

Y. C. CHUNG, Department of Chemistry, Michigan State University, East Lansing, Michigan, 48824; I. SUZUKA, College of Engineering, Nihon University, Koriyama, Fukushima-ken 963, Japan; and G. E. LEROI, Department of Chemistry, Michigan State University, East Lansing, Michigan, 48824.

MG13. PHOTO-THERMAL SPECTROSCOPY OF BENZENE AND PYRIDINE FILMS SUPPORTED ON METAL SURFACES .... 15 min. (4:52)

P. GERAGHTY, M. WIXOM, and A. H. FRANCIS, Department of Chemistry, University of Michigan, Ann Arbor, Michigan, 48109.

MONDAY, JUNE 13, 1983 -- 1:30 P.M.

Room 1008, Evans Chemical Laboratory

Chairman Before Intermission: H. D. BIST, Indian Institute of Technology, Kanpur, India.

Chairman After Intermission: RUSSELL H. BARNES, Battelle Columbus Laboratories, Columbus, Ohio.

MH1. FAR-INFRARED AND RESONANCE RAMAN SPECTRA OF POLYHALIDES....................15 min.(1:30)

E. M. NOUR, L.-H. CHEN, and J. LAANE, Department of Chemistry, Texas A&M University, College Station, Texas, 77843. Present address of E. M. NOUR, Department of Chemistry, Zagazig University, Zagazig, Egypt.

MH2. THE FAR-INFRARED TORSIONAL SPECTRUM OF METHYL SILANE.......................10 min.(1:47)

H. JAGANNATH, M. WONG, and I. OZIER, Department of Physics, University of British Columbia, Vancouver, British Columbia, V6T 2A6, Canada. Present address of M. WONG-Canada Centre for Remote Sensing, Ottawa, Ontario, K1A OY7, Canada. I. OZIER is on leave (1982-83) at the Herzberg Institute of Astrophysics, National Research Council, 100 Sussex Drive, Ottawa, Ontario, K1A OR6, Canada.

MH3. VIBRATIONAL ANALYSIS AND NORMAL COORDINATE CALCULATIONS OF SOME ALKYL THIOCYANATES AND ISOTHIOCYANATES...15 min.(1:59)

H. L. HEUSEL, J. R. DURIG, J. F. SULLIVAN, Department of Chemistry, University of South Carolina, Columbia, South Carolina, 29208; and S. CRADOCK, Department of Chemistry, University of Edinburgh, EH9 3JJ - Edinburgh, Scotland.

MH4. CONFORMATIONAL BARRIERS TO INTERNAL ROTATION OF 3-FLUOROPROPENE BY FT-IR SPECTROSCOPY...15 min.(2:16)

T. S. LITTLE, J. R. DURIG, and MENGZHANG ZHEN, Department of Chemistry, University of South Carolina, Columbia, South Carolina, 29208.

MH5. ROTATIONAL AND VIBRATIONAL SPECTRUM OF TRANS-1-FLUORO-2-BUTENE.............15 min. (2:31)

T. S. LITTLE, J. R. DURIG, and MENGZHANG ZHEN, Department of Chemistry, University of South Carolina, Columbia, South Carolina, 29208.

MH6. THE VIBRATIONAL SPECTRUM AND STRUCTURE OF HEXAFLUOROACETONE................15 min.(2:48)

D.A.C. COMPTON, J. D. GODDARD, S. C. HSI, W. F. MURPHY, and D. M. RAYNER, Division of Chemistry, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A OR6, Canada. Present address of D.A.C. COMPTON-The Standard Oil Company(Ohio), Research and Development Department, Cleveland, Ohio, 44128; Present address of J. D. GODDARD-Department of Chemistry, University of Guelph, Guelph, Ontario, N1G 2W1, Canada; and present address of S. C. HSI-Institute of Applied Chemistry, Chinese Academy of Sciences, Chanchun, China.

Intermission

MH7. THEORETICAL STUDY OF THE CONFORMATIONAL PROPERTIES AND TORSIONAL POTENTIAL FUNCTIONS OF METHACRYLOYL FLUORIDE..............................10 min.(3:15)

B. LASKOWSKI, Analatom Incorporated, 253 Humboldt Court, Sunnyvale, California, 94035; R. JAFFE, NASA, Ames Research Center, Moffett Field, California, 94035; and A. KOMORNICKI, Polyatomics Research Institute, 1101 San Antonio Road, Suite 420, Mountain View, California, 94043.

MH8. VIBRATIONAL SPECTRA AND CONFORMATIONS OF (CYANOMETHYL) CYCLOPROPANE AND DICYCLOPROPYLMETHANE...15 min.(3:27)

V. F. KALASINSKY, J. L. POOL, Department of Chemistry, Mississippi State University, Mississippi State, Mississippi, 39762; Y. Y. YEH, Department of Chemistry, University of Missouri, Kansas City, Missouri, 64110; and C. J. WURREY, Department of Chemistry, University of California - San Diego, La Jolla, California, 92037.

MH9. VIBRATIONAL SPECTRA AND CONFORMATIONS OF (IODOMETHYL) CYCLOPROPANE DERIVATIVES..10 min.(3:42)

V. F. KALASINSKY, Department of Chemistry, Mississippi State University, Mississippi State, Mississippi, 39762; Y. Y. YEH, Department of Chemistry, University of Missouri, Kansas City, Missouri, 64110; and C. J. WURREY, Department of Chemistry, University of California-San Diego, La Jolla, California, 92037.

MH10. VIBRATIONAL SPECTRA AND CONFORMATIONS OF 2-FLUOROETHYLAMINE................15 min.(3:54)

J. A. SMITH and V. F. KALASINSKY, Department of Chemistry, Mississippi State University, Mississippi State, Mississippi, 39762.

MH11. EVIDENCE FOR ANHARMONIC SKELETAL DEFORMATIONS IN A SERIES OF BICYCLO[2.2.1] HEPTANES AND BICYCLO[3.2.1]OCTANES..15 min.(4:11)

H. WIESER, N. IBRAHIM, T. L. SMITHSON, and P. J. KRUEGER, Department of Chemistry, University of Calgary, Calgary, Alberta, T2N 1N4, Canada.

MH12. FT-FAR INFRARED VAPOR PHASE SPECTRA AND INVERSION BARRIERS OF A SERIES OF CYCLOHEXANE AND CYCLOHEXENE DERIVATIVES..................................15 min.(4:28)

H. WIESER, N. IBRAHIM, T. L. SMITHSON, and P. J. KRUEGER, Department of Chemistry, University of Calgary, Calgary, Alberta, T2N 1N4, Canada.

MH13. A COMPARISON OF APPROACHES FOR SOLUTIONS TO THE COUPLED TWO-DIMENSIONAL ANHARMONIC OSCILLATOR...15 min.(4:45)

T. L. SMITHSON, H. WIESER, R. PAUL, Department of Chemistry, University of Calgary, Calgary, Alberta, T2N 1N4, Canada; and F. W. BIRSS, Department of Chemistry, University of Alberta, Edmonton, Alberta, T6G 2G2, Canada.

TUESDAY, JUNE 14, 1983 -- 8:30 A.M.

Room 1153, Physics Laboratory

Chairperson: ROMOLA D'CUNHA, Department of Physics, The Ohio State University, Columbus, Ohio.

TA1. HETERODYNE FREQUENCY MEASUREMENTS FOR INFRARED CALIBRATION TABLES; CO, N_2O, OCS, ETC........20 min.(8:30)

C. R. POLLOCK, School of Electrical Engineering, Cornell University, Ithaca, New York, 14853; F. R. PETERSEN, D. A. JENNINGS, J. S. WELLS, Time and Frequency Division, National Bureau of Standards, Boulder, Colorado, 80303; and A. G. MAKI, Molecular Spectroscopy Division, National Bureau of Standards, Washington, D.C., 20234.

TA2. HIGH RESOLUTION INFRARED SPECTRA OF HIGH TEMPERATURE DIATOMICS........15 min.(8:52)

A. G. MAKI and F. J. LOVAS, Molecular Spectroscopy Division, National Bureau of Standards, Washington, D.C., 20234.

TA3. DIFFERENCE FREQUENCY LASER SPECTROSCOPY OF OD AND OH: SIMULTANEOUS FIT OF THE INFRARED AND MICROWAVE LINES........10 min.(9:09)

T. AMANO, Herzberg Institute of Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A OR6, Canada.

TA4. EXPERIMENTAL DETERMINATION TO LARGE INTERNUCLEAR SEPARATION OF THE $^1\Sigma^+$ STATE ELECTRIC DIPOLE MOMENT FUNCTION OF CO........15 min.(9:21)

C. CHACKERIAN, JR., NASA-Ames Research Center, Astrophysical Experiments Branch, Moffett Field, California, 94035; R. FARRENQ, G. GUELACHVILI, C. ROSSETTI, Laboratoire d'Infrarouge, Université de Paris-Sud, Campus d'Orsay, 91405 Orsay, France; and W. URBAN, Institut für Angewandte Physik der Universität Bonn, D-5300 Bonn 1, West Germany.

TA5. FAR-INFRARED LASER MAGNETIC RESONANCE SPECTROSCOPY OF THE PD($^3\Sigma^-$) RADICAL...10 min.(9:38)

N. OHASHI, Department of Physics, Faculty of Sciences, Kanazawa University, Kanazawa 920, Japan; K. KAWAGUCHI, and EIZI HIROTA, Institute for Molecular Science, Okazaki 444, Japan.

Intermission

TA6. OBSERVATION OF INFRARED SiH IN A SiH_4 PLASMA........15 min.(10:05)

P. CHOLLET, G. GUELACHVILI, M. MORILLON, Laboratoire d'Infrarouge, Université de Paris-Sud, 91405 Orsay, France; P. GRESSIER, G. DE ROSNY, and J. SCHMITT, Equipe de Synthèse des Couches Minces pour l'Energétique, L.P.N.H.E., Ecole Polytechnique, 91128 Palaiseau, France.

TA7. DIPOLE MOMENT OF THE FO RADICAL........15 min.(10:22)

A.R.W. MCKELLAR, Herzberg Institute of Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A OR6, Canada.

TA8. OBSERVATION OF THE ν_1 BAND OF DO_2 BY DIFFERENCE FREQUENCY SPECTROSCOPY......15 min.(10:39)

K. G. LUBIC and T. AMANO, Herzberg Institute of Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A OR6, Canada.

TA9. DETECTION OF THE ν_2 BANDS OF CD_2 AND CH_2 BY INFRARED DIODE LASER SPECTROSCOPY........15 min.(10:56)

A.R.W. MCKELLAR, Herzberg Institute of Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A OR6, Canada; CHIKASHI YAMADA, and EIZI HIROTA, Institute for Molecular Science, Okazaki 444, Japan.

TA10. LASER MAGNETIC RESONANCE OF GERMANIUM CONTAINING SPECIES........15 min.(11:13)

T. J. SEARS, A.R.W. MCKELLAR, Herzberg Institute of Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A OR6, Canada; and M. WONG, Canada Centre for Remote Sensing, 2464 Sheffield Road, Ottawa, Ontario, K1A OY7, Canada.

TA11. OBSERVATION OF ν_2 FCO WITH CO_2 LASER MAGNETIC RESONANCE........15 min.(11:30)

W. J. MCCOY, R. E. MUENCHAUSEN, and G. W. HILLS, Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina, 27514.

TA12. HIGH RESOLUTION FOURIER TRANSFORM SPECTROSCOPY OF THE ν_2 AND ν_3 BANDS OF FNO........15 min.(11:47)

S. C. FOSTER and J.W.C. JOHNS, Herzberg Institute of Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A OR6, Canada.

TUESDAY, JUNE 14, 1983 -- 8:30 A.M.

Room 1009, Physics Laboratory

Chairman: J. A. COXON, Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada.

TB1. THE LOW LYING ELECTRONIC STATES OF CeO, PrO, EuO, AND YbO..................15 min.(8:30)

M. DULICK, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139; R. F. BARROW, Physical Chemistry Laboratory, Oxford University, Oxford, England; C. LINTON, Department of Physics, University of New Brunswick, Fredericton, New Brunswick, E3B 5A3, Canada; S. MC DONALD, S. RICE, and R. W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139.

TB2. ENERGY LINKAGE OF THE SINGLET AND TRIPLET MANIFOLDS IN LaF.................15 min.(8:47)

H. SCHALL, R. W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139; and C. LINTON, Department of Physics, University of New Brunswick, Fredericton, New Brunswick, E3B 5A3, Canada.

TB3. THE LOW LYING ELECTRONIC STATES OF HOLMIUM OXIDE............................15 min.(9:04)

Y. C. LIU, Department of Physics, University of New Brunswick, Fredericton, E3B 5A3, Canada; H. SCHALL, R. W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139; and C. LINTON, Department of Physics, University of New Brunswick, Fredericton, New Brunswick, E3B 5A3, Canada.

TB4. THE ELECTRONIC STRUCTURE OF THE LnX AND LnX^+ (X = O,H,F,Cl,Br,I) MOLECULES..15 min.(9:21)

S. F. RICE, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139; M. DULICK, Department of Chemistry, University of British Columbia, Vancouver, British Columbia, V6T 1Y6, Canada; and R. W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139.

TB5. IMPROVED VIBRATIONAL CONSTANTS OF ScO, YO AND LaO..........................15 min.(9:38)

CARLOS B. SUAREZ, Department of Physics, University of La Plata and Conicet, 1900 La Plata, Argentina.

Intermission

TB6. CURRENT WORK ON THE ANALYSIS OF THE CHEMILUMINESCENCE FROM LEAD OXIDE.......15 min.(10:10)

E. A. DORKO, J. W. GLESSNER, and L. L. RUTGER, Department of Engineering Physics, Air Force Institute of Technology, Wright-Patterson Air Force Base, Ohio, 45433.

TB7. A ROTATIONAL ANALYSIS OF THE C $^1\Pi$ - X $^1\Sigma^+$ SYSTEM OF InCl...................10 min.(10:27)

S. KING, W. B. GRIFFITH, and C. W. MATHEWS, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.

TB8. VIBRATIONAL AND ROTATIONAL ANALYSIS OF HIGH LYING VIBRATIONAL BANDS OF THE BaO A' Σ^+ AND A' $^1\Sigma$ STATES...15 min.(10:39)

NICK FURIO, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania, 19104; and J. GARY PRUETT, The Standard Oil Company (Ohio), Corporate Research Center, 4440 Warrensville Center Road, Warrensville Heights, Ohio, 44128.

TB9. SPARSE MAPPING OF HIGH LYING EXCITED ELECTRONIC STATES IN BaO..............15 min.(10:56)

YEN CHU HSU and J. GARY PRUETT, The Standard Oil Company (Ohio), Corporate Research Center, 4440 Warrensville Center Road, Warrensville Heights, Ohio, 44128.

TB10. Σ8 will be presented here(A. S-C. CHEUNG).................................15 min.(11:13)

TB11. Π1 will be presented here (DAVID O. HARRIS)................................15 min.(11:30)

TB12. Π12 will be presented here (H. PETEK).......................................15 min.(11:47)

TUESDAY, JUNE 14, 1983 -- 8:30 A.M.

Room 1005, Physics Laboratory

Chairman: ROBERT NORDSTROM, Battelle Columbus Laboratories, Columbus, Ohio.

TC1. THEORETICAL STUDIES ON THE ENERGY LEVEL DIAGRAM OF THE CHLOROPHYLL a DIMER....................15 min.(8:30)

L. V. HALEY and J. A. KONINGSTEIN, Department of Chemistry, Carleton University, Ottawa, Ontario, K1S 5B6, Canada.

TC2. EXCITED STATE AND VIBRATIONAL GROUND STATE STUDIES OF CAROTENES AND CHLOROPHYLL MONOMERS AND DIMERS........... Specially Arranged.............30 min.(8:47)

A. DE WILTON, L. V. HALEY, and J. A. KONINGSTEIN, Department of Chemistry, Carleton University, Ottawa, Ontario, K1S 5B6, Canada.

TC3. TIME RESOLVED AND FREQUENCY SELECTIVE FLUORESCENCE OF THE CHL a DIMER.......15 min. (9:20)

A. DE WILTON and J. A. KONINGSTEIN, Department of Chemistry, Carleton University, Ottawa, Ontario, K1S 5B6, Canada.

TUESDAY, JUNE 14, 1983 -- 9:35 A.M.

Room 1005, Physics Laboratory

Chairman: Robert Nordstrom, Battelle Columbus Laboratories, Columbus, Ohio.

TC'1. PHOTOACOUSTIC STUDY OF VIBRATIONAL OVERTONES IN POLYATOMIC MOLECULES........15 min.(9:55)

HOWARD L. FANG, DONNA M. MEISTER, and ROBERT L. SWOFFORD, The Standard Oil Company (Ohio), Corporate Research Center, 4440 Warrensville Center Road, Warrensville Heights, Ohio, 44128.

TC'2. PHOTOACOUSTIC SPECTROSCOPY OF NON-EQUIVALENT METHYL C-H OVERTONE VIBRATIONS....................15 min.(10:12)

HOWARD L. FANG, DONNA M. MEISTER, and ROBERT L. SWOFFORD, The Standard Oil Company (Ohio), Corporate Research Center, 4440 Warrensville Center Road, Warrensville Heights, Ohio, 44128.

TC'3. α-METHYL C-H BOND STRENGTH: A MO ANALYSIS....................15 min.(10:29)

A. B. ANDERSON, D. GERVASIO, Department of Chemistry, Case Western Reserve University, Cleveland, Ohio, 44106; HOWARD L. FANG, DONNA M. MEISTER, and ROBERT L. SWOFFORD, The Standard Oil Company (Ohio), Corporate Research Center, 4440 Warrensville Center Road, Warrensville Heights, Ohio, 44128.

TC'4. PHOTOACOUSTIC STUDY OF OVERTONE STRUCTURE OF METHANOL AND METHANOL-OD.......15 min.(10:46)

HOWARD L. FANG, DONNA M. MEISTER, and ROBERT L. SWOFFORD, The Standard Oil Company (Ohio), Corporate Research Center, 4440 Warrensville Center Road, Warrensville Heights, Ohio, 44128.

TC'5. COMBINATION BANDS IN THE O-H OVERTONE SPECTRA OF METHANOL: THEORY..........15 min.(11:03)

MARTIN L. SAGE, Department of Chemistry, Syracuse University, Syracuse, New York, 13210.

TC'6. THE VISIBLE PHOTOACOUSTIC SPECTRA OF VAPOR-PHASE METHANE AND DEUTERATED METHANES AT 77 K....................15 min.(11:20)

G. J. SCHERER, K. K. LEHMANN, and W. KLEMPERER, Department of Chemistry, Harvard University, Cambridge, Massachusetts, 02138.

TUESDAY, JUNE 14, 1983 -- 1:30 P.M.

Room 1153, Physics Laboratory

Chairman before Intermission: JOSEPH P. SATTLER, U. S. Army Electronics Research and Development, Harry Diamond Laboratories, Adelphi, Maryland.

Chairman after Intermission: R. L. HAWKINS, Department of Physics, The Ohio State University, Columbus, Ohio.

TE1. THE STORY OF THE AMMONIA MOLECULE: 10 YEARS OF INVESTIGATION OF MOLECULAR INVERSION.....................INVITED PAPER..................... 40 min.(1:30)

D. PAPOUSEK, *The J. Heyrovský Institute of Physical Chemistry and* Electrochemistry, Czechoslovak Academy of Sciences, Prague, Czechoslovakia.

TE2. SUB-DOPPLER SPECTROSCOPY IN THE ν_2, ν_4, AND $2\nu_2$ BANDS OF NH_3................15 min.(2:15)

W. H. WEBER and R. W. TERHUNE, Department of Physics, Research and Engineering Staff, Ford Motor Company, Dearborn, Michigan, 48121.

TE3. THE LINESHAPES OF INFRARED-MICROWAVE TWO-PHOTON TRANSITIONS: THE ν_2 BAND OF $^{15}NH_3$...15 min.(2:32)

S. T. SANDHOLM, N. SHABESTARY, and R. H. SCHWENDEMAN, Department of Chemistry, Michigan State University, East Lansing, Michigan, 48824.

TE4. INFRARED-MICROWAVE TWO-PHOTON SPECTRA IN THE ν_4 AND ν_6 BANDS OF CD_2CO.......15 min.(2:49)

K. NAKAGAWA and R. H. SCHWENDEMAN, Department of Chemistry, Michigan State University, East Lansing, Michigan, 48824.

Intermission

TE5. DIODE LASER MEASUREMENTS OF LINE STRENGTHS AND LORENTZ HALF-WIDTHS FOR SOME LINES OF $^{14}NH_3$, $^{15}NH_3$, AND $H_2{}^{16}O$ IN THE 6.6 μm SPECTRAL REGION.........15 min.(3:20)

V. MALATHY DEVI, B. FRIDOVICH, D.G.S. SNYDER, G. D. JONES, NOAA/NESDIS, FOB #4, E/RA21, Washington, D.C., 20233; and K. NARAHARI RAO, Department of Physics, The Ohio State University, Columbus, Ohio, 43210.

TE6. EXPERIMENTAL AND THEORETICAL INVESTIGATION OF FOREIGN GAS BROADENING OF AMMONIA TRANSITIONS OF THE $\nu_2(1 - 0)$ AND $\nu_2(2 - 1)$ BANDS....................10 min.(3:37)

G. BALDACCHINI, ENEA, Dip. TIB-FIS, Laboratorio Spettroscopia Molecolare, 00044 Frascati, Rome, Italy; S. MARCHETTI, C.N.R., Pisa, Italy; V. MONTELATICI, V. SORGE, ENEA, Dip. TIB-FIS, Laboratorio Spettroscopia Molecolare, 00044 Frascati, Rome, Italy; G. BUFFA, and O. TARRINI, Istituto di Fisica, Università di Pisa, Pisa, Italy.

TE7. MEASUREMENTS OF THE ν_3 BAND OF HCN BROADENED BY N_2 AND BY HF................10 min.(3:49)

M.A.H. SMITH and G. A. HARVEY, NASA Langley Research Center, Mail Stop 401A, Hampton, Virginia, 23665.

TE8. HIGH RESOLUTION LINE INTENSITY MEASUREMENTS OF THE $\nu_4 + \nu_5$ BAND OF C_2H_2.....15 min.(4:01)

J. PODOLSKE, M. LOEWENSTEIN, Space Science Division, NASA Ames Research Center, Moffett Field, California, 94035; and P. VARANASI, Laboratory for Planetary Atmospheres Research, State University of New York, Stony Brook, New York, 11794.

TE9. MEASUREMENT OF INTENSITIES IN THE ν_4 FUNDAMENTAL BAND OF $^{13}CH_4$ AT 153 K AND 296 K...10 min.(4:18)

P. VARANASI, Laboratory for Planetary Atmospheres Research, State University of New York, Stony Brook, New York, 11794; L. P. GIVER, and F.P.J. VALERO, Astrophysical Experiments Branch, NASA-Ames Research Center, Moffett Field, California, 94035.

TE10. NITROGEN-BROADENING OF THE INFRARED LINES OF $^{12}CH_4$, $^{13}CH_4$ AND $^{12}CH_3D$ AT LOW TEMPERATURES...15 min.(4:30)

P. VARANASI, Laboratory for Planetary Atmospheres Research, State University of New York, Stony Brook, New York, 11794; L. P. GIVER, and F.P.J. VALERO, Astrophysical Experiments Branch, NASA-Ames Research Center, Moffett Field, California, 94035.

TE11. EXPERIMENTAL COLLISION-BROADENED LINEWIDTHS IN METHANE.....................10 min.(4:47)

J. W. BRAULT, Kitt Peak National Observatory, Tucson, Arizona, 85726;
K. FOX, Department of Physics and Astronomy, University of Tennessee,
Knoxville, Tennessee, 37996; D. E. JENNINGS, Goddard Space Flight
Center, Greenbelt, Maryland, 20771; J. S. MARGOLIS and L. R. BROWN,
Jet Propulsion Laboratory, Pasadena, California, 91103.

TE12. THEORETICAL STUDIES OF COLLISION-BROADENED LINEWIDTHS IN METHANE...........10 min.(4:59)

KENNETH FOX, Department of Physics and Astronomy, University of
Tennessee, Knoxville, Tennessee, 37996.

TUESDAY, JUNE 14, 1983 -- 2:15 P.M.

Room 1009, Physics Laboratory

Chairman: P. L. JONES, Department of Chemistry, The Ohio State University, Columbus, Ohio.

TF1. HIGH SENSITIVITY HETERODYNE-POLARIZATION SPECTROSCOPY......................15 min.(2:15)

M. RAAB and A. WEBER, Molecular Spectroscopy Division, National Bureau of Standards, Washington, D.C., 20234.

TF2. RADIATIVE TRANSITION PROBABILITIES AND DIPOLE MOMENTS FOR ALL VIBRATIONAL LEVELS IN THE X $^1\Sigma^+$ AND A $^1\Sigma^+$ STATES OF NaH................................10 min.(2:32)

W. T. ZEMKE, Department of Chemistry, Wartburg College, Waverly, Iowa, 50677; and W. C. STWALLEY, Iowa Laser Facility, University of Iowa, Iowa City, Iowa, 52242.

TF3. CRITICAL COMPILATION OF SPECTROSCOPIC DATA FOR THE ALKALI METAL HYDRIDE MOLECULES..15 min.(2:44)

W. C. STWALLEY, Iowa Laser Facility and Department of Chemistry, University of Iowa, Iowa City, Iowa, 52242; and S. C. YANG, Department of Chemistry, University of Rhode Island, Providence Rhode Island, 02881.

Intermission

TF4. CRITICAL COMPILATION OF SPECTROSCOPIC DATA FOR THE ALKALI METAL DIATOMIC MOLECULES..15 min.(3:15)

W. C. STWALLEY, Iowa Laser Facility and Departments of Chemistry and Physics, University of Iowa, Iowa City, Iowa, 52242; W. T. ZEMKE, Department of Chemistry, Wartburg College, Waverly, Iowa, 50677; and R. B. BERNHEIM, Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania, 16802.

TF5. NEW OPTICALLY-PUMPED ALKALI METAL DIATOMIC LASERS...........................15 min.(3:32)

J. T. BAHNS, Iowa Laser Facility, University of Iowa, Iowa City, Iowa, 52242; A. R. RAJAEI-RIZI, Department of Chemistry, Drexel University, Philadelphia, Pennsylvania, 19104; K. K. VERMA, 3B-611A, Bell Telephone Laboratory, Holmdel, New Jersey, 07733; F. B. ORTH, MHD Energy Center, Mississippi State University, Mississippi State, Mississippi, 39762; and W. C. STWALLEY, Iowa Laser Facility, University of Iowa, Iowa City, Iowa, 52242.

TF6. LASER EXCITED FLUORESCENCE OF Na_2: INTENSITIES IN THE A-X AND B-X TRANSITIONS...10 min. CANCELLED

K. S. CHANDRASEKHAR, T. K. BALASUBRAMANIAN, K. RAGHUVEER, and N. A. NARASIMHAM, Spectroscopy Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India.

TF7. METHOD FOR CALCULATING HIGH-ORDER RKR POTENTIAL............................15 min.(3:49)

R. J. LE ROY, Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Ontario, N2L 3G1, Canada; and P. PAJUNEN, Department of Chemistry, University of Oulu, Linnanmaa, 90570 Oulu 57, Finland.

TF8. OPTICALLY DETECTED MAGNETIC RESONANCE OF SEVERAL CARBONYL COMPOUNDS ADSORBED ON ALUMINA..10 min.(4:06)

A. M. NISHIMURA, Department of Chemistry, Westmont College, Santa Barbara, California, 93108.

TF9. INFRA RED OPTICAL DOUBLE RESONANCE SPECTROSCOPY OF ND_2......................15 min.(4:18)

R. E. MUENCHAUSEN and G. W. HILLS, Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina, 27514.

TF10. OPTOGALVANIC SPECTROSCOPY IN LOW PRESSURE DISCHARGES WITH COLOR-CENTER AND DYE LASERS...10 min.(4:35)

R. D. MAY, Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina, 27514; Z. ZHU, Department of Physics, Dalian Institute of Technology, Dalian, Liaoning 116024, China; and G. W. HILLS, Department of Chemistry, The University of North Carolina, Chapel Hill, North Carolina, 27514.

TF11. Σ14 will be presented here(M. C. HEAVEN)..................................10 min.(4:47)

TF12. Π2 will be presented here (LI LI)..10 min.(4:59)

TUESDAY, JUNE 14, 1983 -- 2:15 P.M.

Room 1005, Physics Laboratory

Chairman: ZHU QINGSHI, Salt Lake Institute of Chinese Academy of Science, Sining, Qinghai, People's Republic of China.

TG1. SOME MICROWAVE AND INFRARED OBSERVATIONS ON THE METHANOL C-O STRETCH STATE .... 15 min.(2:15)

R. M. LEES, P. MCGHEE, R.R.J. GOULDING, and I. MUKHOPADHYAY, Department of Physics, University of New Brunswick, Fredericton, New Brunswick, E3B 5A3, Canada.

TG2. FOURIER TRANSFORM INFRARED SPECTRUM OF METHYLAMINE FROM 50-125 CM^{-1} .... 15 min.(2:32)

M. S. MALGHANI, R. M. LEES, and R. T. ADSETT, Department of Physics, University of New Brunswick, Fredericton, New Brunswick, E3B 5A3, Canada.

TG3. MICROWAVE SPECTRA OF PERFLUOROETHYLENE OXIDE .... 10 min.(2:49)

J. AGOPOVICH, Charles Stark Draper Laboratory, 555 Technology Square, Cambridge, Massachusetts, 02139; C. GILLIES, and T. RAW, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York, 12181.

TG4. MICROWAVE SPECTRA OF TRANS-1,2-DIFLUOROETHYLENE OXIDE .... 15 min.(3:01)

G. LABRECQUE, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York, 12181; J. AGOPOVICH, Charles Stark Draper Laboratory, 555 Technology Square, Cambridge, Massachusetts, 02139; and C. GILLIES, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York, 12181.

Intermission

TG5. MICROWAVE SPECTRUM OF CH_2DSH .... 15 min.(3:35)

CHUN FU SU and C. RICHARD QUADE, Department of Physics, Texas Tech University, Lubbock, Texas, 79409.

TG6. HIGH RESOLUTION SPECTROSCOPY OF VIBRATIONALLY EXCITED FLUOROFORM-D BY HETERODYNE FREQUENCY MEASUREMENT OF SMMW LASER EMISSION .... 10 min.(3:52)

M. S. TOBIN, R. P. LEAVITT, T. W. DALEY, and W. G. TRUEHEART, JR., U. S. Army Electronics Research and Development Command, Harry Diamond Laboratories, 2800 Powder Mill Road, Adelphi, Maryland, 20783.

TG7. ROTATIONAL SPECTRA OF 16-17-16 AND 17-16-16 O_3 .... 10 min.(4:04)

E. A. COHEN and H. M. PICKETT, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, 91109.

TG8. ROTATIONAL SPECTRA OF VIBRATIONALLY EXCITED OZONE .... 10 min.(4:16)

H. M. PICKETT and E. A. COHEN, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, 91109.

TG9. Σ1 will be presented here (A. B. MOHAMAD) .... 10 min.(4:28)

TG10 Π11 will be presented here (G. O. BRINK) .... 15 min.(4:40)

TUESDAY, JUNE 14, 1983 -- 2:15 P.M.

Room 1008, Evans Chemical Laboratory

Chairman: P. L. POLAVARAPU, Department of Chemistry, Vanderbilt University, Nashville, Tennessee.

TH1. A KINETIC STUDY OF THE THERMAL DECOMPOSITION OF 2,2,4,4-TETRAMETHYLCYCLOBUTANEDIONE USING TIME-RESOLVED FTIR........................15 min.(2:15)

DAVID LATHAM, J. BAIARDO, R. MUKHERJEE, S. PASZYC, and M. VALA, Department of Chemistry, University of Florida, Gainesville, Florida, 32611.

TH2. FOURIER TRANSFORM INFRARED SPECTRA OF $2NH_3 \cdot D_2O$ AND $2ND_3 \cdot H_2O$, AT 15°K........15 min.(2:32)

JOHN E. BERTIE, Department of Chemistry, The University of Alberta, Edmonton, Alberta, T6G 2G2, Canada; and J. P. DEVLIN, Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma, 74074.

TH3. VIBRATIONAL SPECTRA OF SOLID $CF_3C\ell$, $CF_2C\ell_2$ AND $CFC\ell_3$........................15 min.(2:49)

D. D. FONTAINE and G. E. LEROI, Department of Chemistry, Michigan State University, East Lansing, Michigan, 48824.

TH4. FAR INFRARED SPECTRUM OF THE LOW-TEMPERATURE PHASE OF SOLID $CC\ell_4$............10 min.(3:06)

D. D. FONTAINE and G. E. LEROI, Department of Chemistry, Michigan State University, East Lansing, Michigan, 48824.

TUESDAY, JUNE 14, 1983 -- 3:30 P.M.

Room 1008, Evans Chemical Laboratory

Chairman: P. L. POLAVARAPU, Department of Chemistry, Vanderbilt University, Nashville, Tennessee.

TH'1. ESR OF Cr METAL MOLECULES AT 4°K...15 min.(3:30)

R. J. VAN ZEE, Department of Chemistry, University of Florida, Gainesville, Florida, 32611; C. A. BAUMANN, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405; and W. WELTNER, JR., Department of Chemistry, University of Florida, Gainesville, Florida, 32611.

TH'2. ESR OF PSEUDOROTATING $^6Li_3$ AND $^7Li_3$..15 min.(3:47)

D. A. GARLAND and D. M. LINDSAY, Department of Chemistry, City University of New York, The City College, New York, New York, 10031.

TH'3. TWO-PHOTON SPECTROSCOPY OF Cu^+ IN ALKALI HALIDE HOST CRYSTALS..............15 min.(4:04)

STEPHEN A. PAYNE, ANDREA GOLDBERG, and DONALD S. MCCLURE, Department of Chemistry, Princeton University, Princeton, New Jersey, 08544.

TH'4. EXCITED STATE DYNAMICS OF Cu^+ IN NaF HOST CRYSTAL..........................15 min.(4:21)

ANDREA GOLDBERG, STEPHEN A. PAYNE, and DONALD S. MCCLURE, Department of Chemistry, Princeton University, Princeton, New Jersey, 08544.

TH'5. Σ3 will be presented here (W.-H. CHEN)....................................10 min.(4:38)

TH'6. Σ4 will be presented here (J. D. SCOTT)...................................15 min.(4:50)

WEDNESDAY, JUNE 15, 1983 -- 8:45 A.M.

Auditorium, Independence Hall

Chairman: K. NARAHARI RAO, Department of Physics, The Ohio State University, Columbus, Ohio.

Plenary Session

WA1. MOLECULAR HYDROGEN IN THE LABORATORY AND IN SPACE........40 min.

G. HERZBERG, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A OR6.

WA2. STRUCTURE AND DYNAMICS OF MEMBRANE ASSEMBLIES BY RAMAN SPECTROSCOPY......................................40 min.

IRA W. LEVIN, Section on Molecular Biophysics, Laboratory of Chemical Physics, National Institute of Arthritis, Diabetes, and Digestive and Kidney Diseases, National Institutes of Health, Bethesda, Maryland, 20205.

Intermission

WA3. STUDY OF CHEMICAL TRANSIENTS BY TIME-RESOLVED INFRARED SPECTRAL PHOTOGRAPHY...........................40 min.

PETER P. SOROKIN (COBLENTZ SOCIETY LECTURER) IBM, Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York, 10598.

WEDNESDAY, JUNE 15, 1983 -- 1:30 P.M.

Room 1153, Physics Laboratory

Chairperson Before Intermission: D. BAILLY, Laboratoire d'Infrarouge, Université de Paris-Sud, 91405 Orsay, France.

Chairman After Intermission: D. F. EGGERS, Department of Chemistry, University of Washington, Seattle, Washington.

WE1. HUND'S COUPLING CASES AND TETRAHEDRAL SPLITTINGS IN ROTATIONAL LEVELS OF ELECTRONIC $^2F_2$ STATES IN ND_4 .... 15 min.(1:30)

G. HERZBERG, Herzberg Institute of Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A OR6, Canada; and J. T. HOUGEN, Molecular Spectroscopy Division, National Bureau of Standards, Washington, D.C., 20234.

WE2. LOCAL MODE BEHAVIOR IN THE STRETCHING OVERTONES OF GERMANE .... 15 min.(1:47)

A. G. ROBIETTE, Department of Chemistry, University of Reading, Whiteknights, Reading, England, RG6 2AD; A. S. PINE, Molecular Spectroscopy Division, National Bureau of Standards, Washington, D.C., 20234; and S. J. DAUNT, Department of Chemistry, Concordia University, Montreal, Quebec, H3G 1M8, Canada and Molecular Spectroscopy Laboratory, Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee, 37996.

WE3. COMBINATIONS AND OVERTONES OF CF_4 .... 15 min.(2:04)

A. S. PINE, Molecular Spectroscopy Division, National Bureau of Standards, Washington, D.C., 20234; and A. G. ROBIETTE, Department of Chemistry, University of Reading, Whiteknights, Reading, England, RG6 2AD.

WE4. LINE STRENGTHS OF THE ν_2 AND ν_4 BANDS OF $^{12}CH_4$ .... 10 min.(2:21)

M. LOETE and J. C. HILICO, Laboratoire de Spectronomie Moléculaire, 21100 Dijon, France.

WE5. THEORETICAL AND EXPERIMENTAL STUDY OF LINE STRENGTHS IN THE $\nu_3 - \nu_4$ HOT BAND OF METHANE .... 10 min.(2:33)

J. C. HILICO, M. LOETE, Laboratoire de Spectronomie Moléculaire, 21100 Dijon, France; and L. R. BROWN, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, 91109.

WE6. THE ANHARMONIC CONSTANTS AND FORCE FIELD OF SF_6 .... 15 min.(2:45)

B. J. KROHN, R. S. MCDOWELL, J. L. LYMAN, University of California, Los Alamos National Laboratory, Los Alamos, New Mexico, 87545; and J. OVEREND, Department of Chemistry, University of Minnesota, Minneapolis, Minnesota, 55455.

Intermission

WE7. PERTURBATIVE APPROXIMATIONS IN THE ANALYSIS OF FUNDAMENTAL BANDS OF SPHERICAL-TOP MOLECULES .... 15 min.(3:15)

B. J. KROHN, University of California, Los Alamos National Laboratory, Theoretical Division, Los Alamos, New Mexico, 87545; and J.K.G. WATSON, Herzberg Institute of Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa, K1A 0R6, Canada.

WE8. DIODE AND DIFFERENCE-FREQUENCY LASER SPECTRA OF CUBANE................ .....10 min.(3:32)

A. S. PINE, A. G. MAKI, Molecular Spectroscopy Division, National Bureau of Standards, Washington, D.C., 20234; and A. G. ROBIETTE, Department of Chemistry, University of Reading, Whiteknights, Reading, England, RG6 2AD.

WE9. ORDER, DISORDER, AND CLUSTERING IN ROTOR SPECTRA: A COMPARISON OF SPHERICAL AND ASYMMETRIC TOP DYNAMICS..................................... 15 min.(3:44)

W. G. HARTER, Department of Physics, Georgia Institute of Technology, Atlanta, Georgia, 30332; and C. W. PATTERSON, University of California, Los Alamos National Laboratory, Theoretical Division, Los Alamos, New Mexico, 87545.

WE10. HIGH VIBRATIONAL OVERTONES OF SPHERICAL TOP MOLECULES...................... 15 min.(4:01)

C. W. PATTERSON, University of California, Los Alamos National Laboratory, Theoretical Division, Los Alamos, New Mexico, 87545; and W. G. HARTER, Department of Physics, Georgia Institute of Technology, Atlanta, Georgia, 30332.

WE11. COMPARISON OF THE SYMMETRIZED CARTESIAN AND ANGULAR MOMENTUM BASIS SETS TO DESCRIBE VIBRATIONALLY EXCITED STATES IN SPHERICAL TOP MOLECULES.........15 min.(4:18)

HAROLD B. LEVENE and DAVID S. PERRY, Department of Chemistry, University of Rochester, Rochester, New York, 14627.

WE12. GENERAL HARMONIC FORCE FIELD FOR HYDROGEN PEROXIDE..........................10 min.(4:35)

J. J. HILLMAN, Infrared and Radio Astronomy Branch, NASA-Goddard Space Flight Center, Greenbelt, Maryland, 20771; and J. D. ROGERS, Department of Environmental Science, General Motors Research Laboratories, Warren, Michigan, 48090.

WE13. EFFECTS OF A PERTURBATION ON THE GROUND TORSIONAL-VIBRATIONAL STATE OF HYDROGEN PEROXIDE..10 min.(4:47)

WM. BRUCE OLSON, Molecular Spectroscopy Division, National Bureau of Standards, Washington, D.C., 20234; and ROBERT HUNT, Department of Physics, Florida State University, Tallahassee, Florida, 32306.

WEDNESDAY, JUNE 15, 1983 -- 1:30 P.M.

Room 1009, Physics Laboratory

Chairman: ERNEST A. DORKO, Department of Physics, Air Force Institute of Technology, Wright Patterson Air Force Base, Ohio.

WF1. OBSERVATION OF THE C(3/2) ← X(1/2) TRANSITION IN XeF........................15 min.(1:30)

H. HELM, D. L. HUESTIS, M. J. DYER, and D. C. LORENTS, Molecular Physics Laboratory, Stanford Research Institute International, Menlo Park, California, 94025.

WF2. PHOTOFRAGMENT SPECTROSCOPY OF Cs_2^+..15 min.(1:45)

H. HELM, R. MÖLLER, P. C. COSBY, and D. L. HUESTIS, Molecular Physics Laboratory, Stanford Research Institute International, Menlo Park, California, 94025.

WF3. ROTATIONAL BRANCH STRENGTHS FOR $O_2(A^3\Sigma_u^+ \rightarrow X^3\Sigma_g^-)$............................15 min.(2:00)

D. L. HUESTIS and T. G. SLANGER, Molecular Physics Laboratory, Stanford Research Institute International, Menlo Park, California, 94025.

WF4. INTENSITIES OF FORBIDDEN BAND SYSTEMS OF MOLECULAR OXYGEN..................15 min.(2:18)

C.M.L. KERR and J.K.G. WATSON, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, KlA OR6, Canada.

WF5. PULSED LASER EXCITATION AND PHOTOACOUSTIC DETECTION OF THE 1-0 OXYGEN SCHUMANN-RUNGE BAND..10 min.(2:35)

P. B. KELLY, R. COHEN, R. B. MILES, and J. GELFAND, Applied Physics and Materials Laboratory, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey, 08544.

WF6. HIGH RESOLUTION ABSORPTION CROSS SECTIONS AND BAND OSCILLATOR STRENGTHS OF THE SCHUMANN-RUNGE BANDS OF O_2..15 min.(2:47)

K. YOSHINO, D. E. FREEMAN, J. R. ESMOND, and W. H. PARKINSON, Harvard College Observatory, 60 Garden Street, Cambridge, Massachusetts, 02138.

Intermission

WF7. INTRACAVITY LASER ABSORPTION SPECTROSCOPY - A COMPARISON WITH CLASSICAL ABSORPTION - LINE SHAPES AND QUANTITATIVE MEASUREMENTS.....................10 min.(3:15)

M. CHENEVIER, M. A. MELIERES, and F. STOECKEL, Laboratoire de Spectrometrie Physique, Universite Scientifique et Médicale de Grenoble, BP68, 38042 Saint Martin d'Hères, France.

WF8. TIME EVOLUTION OF SHORT-LIVED MOLECULAR SPECIES OBSERVED BY INTRACAVITY LASER ABSORPTION SPECTROSCOPY...15 min.(3:27)

F. STOECKEL, Laboratoire de Spectrometrie Physique, Universite Scientifique et Médicale de Grenoble, BP68 38042 Saint Martin d'Hères; M. D. SCHUH, Department of Chemistry, Davidson College, Davidson, North Carolina, 28036; and G. H. ATKINSON, Department of Chemistry, Syracuse University, Syracuse, New York, 13210.

WF9. TIME-RESOLVED PHOSPHORESCENCE SPECTRA OF ACETALDEHYDE (CH_3CHO) AND PERDEUTEROACETALDEHYDE VAPORS...10 min.(3:44)

M. D. SCHUH, Department of Chemistry, Davidson College, Davidson, North Carolina, 28036; S. SPEISER, Department of Chemistry, Technion, Haifa, Israel; and G. H. ATKINSON, Department of Chemistry, Syracuse University, Syracuse, New York, 13210.

WF10. IDENTIFICATION OF THE nf COMPLEXES IN N_2 BY UV ABSORPTION..................15 min.(3:56)

E. S. CHANG, Department of Physics and Astronomy, University of Massachusetts, Amherst, Massachusetts, 01003; and K. YOSHINO, Center for Astrophysics, Harvard University, Cambridge, Massachusetts, 02138.

WF11. ANALYSIS OF THE 5g-4f EMISSION LINES IN H_2.................................15 min.(4:11)

E. S. CHANG, S. PULCHTOPEK, Department of Physics and Astronomy, University of Massachusetts, Amherst, Massachusetts, 01003; and E. E. EYLER, Lyman Laboratory of Physics, Harvard University, Cambridge, Massachusetts, 02138.

WF12. ROTATIONAL ANALYSIS OF THE $B^1\Sigma^+ - A^1\Pi$ SYSTEM OF $^{13}C\ ^{18}O$....................10 min. (4:28)

C.V.V. PRASAD, G. L. BHALE, and S. PADDI REDDY, Department of Physics, Memorial University of Newfoundland, St. John's, Newfoundland, A1B 3X7, Canada. G. L. BHALE is on leave from the Bhabha Atomic Research Centre, Bombay, India.

WF13. TWO PHOTON EXCITATION OF THE $D^1\Delta - X^1\Sigma^+$ TRANSITION IN CO....................15 min. (4:40)

C. KITTRELL, S. CAMERON, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139; R. F. BARROW, Physical Chemistry Laboratory, Oxford University, Oxford, England, OX1 3QZ; L. BUTLER, Materials and Molecular Research Division, Lawrence Berkeley Laboratory and Department of Chemistry, University of California, Berkeley, California, 94720; and R. W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139.

WEDNESDAY, JUNE 15, 1983 -- 1:30 P.M.

Room 1005, Physics Laboratory

Chairman: G.N.R. TRIPATHI, Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana.

WG1. RECENT DEVELOPMENTS IN STIMULATED RAMAN METHODS..........40 min.(1:30)

A. OWYOUNG, Advanced Laser Technology, Division 1124, Sandia National Laboratories, Albuquerque, New Mexico, 87185.

WG2. APPLICATIONS OF RESONANCE ENHANCED COHERENT ANTI-STOKES RAMAN SPECTROSCOPY................................30 min.(2:15)

L. A. CARREIRA, Department of Chemistry, The University of Georgia, Athens, Georgia, 30602.

WG3. COLLISIONAL LINE BROADENING AND MIXING IN VIBRATIONAL Q-BRANCH SPECTRA..30 min.(2:48)

GREGORY J. ROSASCO, Temperature and Pressure Measurements and Standards Division, Center for Absolute Physical Quantities, National Bureau of Standards, Washington, D.C., 20234.

Intermission

WG4. NONLINEAR RAMAN SPECTROSCOPY FOR COMBUSTION RESEARCH.....30 min.(3:30)

LARRY A. RAHN, Sandia National Laboratories, Livermore, California, 94550.

WG5. PHOTOACOUSTIC RAMAN SPECTROSCOPY OF GASES................30 min.(4:03)

J. J. BARRETT, Allied Corporation, Electro-Optical Products, 7 Powder Horn Drive, Mt. Bethel, New Jersey, 07060.

WG6. ENERGY TRANSFER EFFECTS ON THE LINESHAPE OF THE NO FUNDAMENTAL RAMAN Q-BRANCH, STUDIED WITH NON-LINEAR RAMAN GAIN..15 min.(4:36)

G. J. ROSASCO, Temperature and Pressure Measurements and Standards Division, Center for Absolute Physical Quantities, National Bureau of Standards, Washington, D.C., 20234, W. LEMPERT, Molecular Spectroscopy Division, National Bureau of Standards, Washington, D.C., 20234; and W. S. HURST, Temperature and Pressure Measurements and Standards Division, Center for Absolute Physical Quantities, National Bureau of Standards, Washington, D.C., 20234.

This special seminar on Non-Linear Raman Spectroscopy has been arranged in collaboration with the Coblentz Society. We are particularly grateful to Dr. R. S. McDowell for his help on behalf of the Society.

WG7. Σ6 will be presented here (R. A. HILL)..................10 min.(4:53)

WEDNESDAY, JUNE 15, 1983 -- 1:30 P.M.

Room 1003, Evans Chemical Laboratory

Chairman: RICHARD F. FIRESTONE, Department of Chemistry, The Ohio State University, Columbus, Ohio.

WH1. ROTATIONAL RELAXATION AND Λ COMPONENT SWITCHING COLLISIONS IN THE BaO A' $^1\Pi$ STATE..15 min.(1:30)

YEN CHU HSU and J. GARY PRUETT, The Standard Oil Company (Ohio), Corporate Research Center, 4440 Warrensville Center Road, Warrensville Heights, Ohio, 44128.

WH2. QUENCHING OF THE $A^2\Sigma^+$ STATE OF OH AT ~1100 K ....15 min.(1:47)

PAUL W. FAIRCHILD, GREGORY P. SMITH, and DAVID R. CROSLEY, Molecular Physics Laboratory, Stanford Research Institute International, Menlo Park, California, 94025.

WH3. INTRAMOLECULAR VIBRATIONAL REDISTRIBUTION AS SEEN IN TIME RESOLVED EMISSION FROM p-DIFLUOROBENZENE..15 min.(2:04)

K. W. HOLTZCLAW, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405; D. A. DOLSON, Environmental Science Department, General Motors Research Laboratories, Warren, Michigan, 48090; and C. S. PARMENTER, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405.

WH4. FLUORESCENCE SPECTRA OF p-DIFLUOROBENZENE IN A MOLECULAR BEAM, EVIDENCE FOR ROTATIONAL INVOLVEMENT IN INTRAMOLECULAR VIBRATIONAL REDISTRIBUTION.....15 min.(2:21)

S. H. LEE and C. S. PARMENTER, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405.

WH5. INTERMOLECULAR POTENTIALS AND VIBRATIONAL ENERGY FLOW IN LIQUIDS: V-T RELAXATION OF CO(v=1) BY H_2, D_2 AND He IN LIQUID Ar........................15 min.(2:38)

DONALD W. LUPO and G. E. EWING, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405.

WH6. VIBRATIONAL ENERGY TRANSFER OF CO BY CH_4, CD_4, AND CF_4 IN LIQUID Ar.........15 min. (2:55)

H. M. ABDEL-HALIM and G. E. EWING, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405.

WH7. DIODE INFRARED LASER DOUBLE RESONANCE OF SUBSTITUTED METHANES: SPECTROSCOPY AND RELAXATION..15 min. (3:12)

J. I. STEINFELD, D. HARRADINE, L. LAUX, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139; and M. DUBS, Physikalisches-Chemisches Institut der Universitat Zurich, CH-8057, Switzerland.

WH8. PHONON-ASSISTED ENERGY TRANSFER IN MOLECULAR CRYSTALS.......................15 min. (3:29)

I. Y. CHAN and M. P. KARNETT, Department of Chemistry, Brandeis University, Waltham, Massachusetts, 02254.

WH9. ?13 will be presented here (R. MOORE).......................................10 min.(3:46)

WEDNESDAY, JUNE 15, 1983 -- 4:00 P.M.

Chairman: J. J. VAN VAALS, Afd. Atoom-en Molekuulfysica, Katholieke Universiteit Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

WH'1. CHEMILUMINESCENT OXIDATION OF ZINC ATOMS BY NITROUS OXIDE..................15 min.(4:05)

BRIAN G. WICKE, Department of Physical Chemistry, General Motors Research Laboratories, Warren, Michigan, 48090.

WH'2. JET SPECTROSCOPY OF PERPROTONATED AND PERDEUTERATED BENZENE DIMERS BY 2-COLOR RESONANCE PHOTOIONIZATION.......................................10 min.(4:22)

K. H. FUNG, Herzberg Institute of Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A OR6, Canada; H. L. SELZLE, and E. W. SCHLAG, Physikalische Chemie der Technischen Universität München, 8046 Garching, West Germany.

WH'3. FTIR SPECTRUM OF BENZENE IN A SUPERSONIC EXPANSION.. ....15 min.(4:34)

D. SNAVELY, V. WALTERS, S. COLSON, and K. WIBERG, Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut, 06511.

WH'4. FTIR SPECTRUM OF PYRIDINE IN A SUPERSONIC EXPANSION........................15 min.(4:51)

V. WALTERS, K. WONG, D. SNAVELY, S. COLSON, and K. WIBERG, Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut, 06511.

THURSDAY, JUNE 16, 1983 -- 8:30 A.M.

Room 1153, Physics Laboratory

Chairman: Jon T. Hougen, National Bureau of Standards, Washington, D.C., 20234

RA1. MODERN ASPECTS OF MOLECULAR VIBRATION-ROTATION THEORY..25 min.(8:30)

M. R. ALIEV, Institute of Spectroscopy, Academy of Sciences, Akademgorodok, Moscow Region, U.S.S.R.

RA2. HIGH RESOLUTION SPECTROSCOPY WITH DIODE LASERS...........25 min.(9:00)

I. I. ZASAVITSKY, P. N. Lebedev Physical Institute, Academy of Sciences, Moscow Region, U.S.S.R.

RA3. SPECTROSCOPY OF ATMOSPHERIC AND POLLUTION GASES..........25 min.(9:30)

YU. S. MAKUSHKIN, Institute of Atmopsheric Optics, Academy of Sciences, Siberian Branch, Tomsk, U.S.S.R.

Intermission

RA4. HIGH-SENSITIVE LASER SPECTROSCOPY IN THE VISIBLE AND IN THE PHOTOGRAPHIC INFRARED.........................25 min.(10:10)

L. N. SINITSA, Institute of Atmospheric Optics, Academy of Sciences, Siberian Branch, Tomsk, U.S.S.R.

RA5. STUDY OF MICROWAVE SPECTRAL LINES: PRESSURE SHIFT, BROADENING, LINESHAPE..................................25 min(10:40)

A. F. KRUPNOV, Institute of Applied Physics, Academy of Sciences, 46 Uljanov Street, 603600 Gorky, U.S.S.R.

RA6. FIRST INFRARED DETECTION OF ATMOSPHERIC NO_2 FROM THE GROUND..15 min.(11:10)

J.-M. FLAUD, C. CAMY-PEYRET, A. PERRIN, Laboratoire de Physique Moleculaire et d'Optique Atmospherique, C.N.R.S., Batiment 221, Campus d'Orsay, 91405 Orsay Cedex, France, J. LAURENT, O N E R A, 92320 Chatillon, France; and G. M. STOKES, Battelle Pacific North West Laboratoires, P.O. Box 999, Richland, Washington, 93352.

RA7. E11 will be presented here (JOAN M. FRYE)..............15 min.(11:27)

THURSDAY, JUNE 16, 1983 -- 9:30 A.M.

Room 1009, Physics Laboratory

Chairman: RUSSELL PITZER, Department of Chemistry, The Ohio State University, Columbus, Ohio.

RB1. A THEORETICAL STUDY OF THE OH MEINEL SYSTEM. THE ORIGIN OF THE SURFACE GLOW ON SPACE VEHICLES?............... INVITED PAPER.......................40 min. (9:30)

STEPHEN R. LANGHOFF, NASA-Ames Research Center, Moffett Field, California, 94035.

RB2. OPTICAL AND MAGNETO-OPTICAL ROTATION DUE TO TRANSVERSE ELECTRONIC MOTION IN THICK HELICES OF NON-INTEGRAL TURNS....................................10 min.(10:15)

SAMUEL H. BROWN, Naval Ship Research and Development Center, Department of the Navy, Annapolis, Maryland, 21402; and YING-NAN CHIU, Department of Chemistry, The Catholic University of America, Washington, D.C., 20064.

RB3. "CRYSTAL FIELD" THEORY FOR THE RYDBERG STATES OF POLYATOMIC MOLECULES AND ORBITAL CORRELATION TO DISSOCIATED FRAGMENTS...........................15 min.(10:27)

YING-NAN CHIU, Department of Chemistry, The Catholic University of America, Washington, D.C., 20064.

RB4. DEGENERATE STATES IN OPTICAL ROTATION.....................................10 min.(10:44)

YING-NAN CHIU, Department of Chemistry, The Catholic University of America, Washington, D.C., 20064 and Institute of Chemistry, Academia Sinica, Nankang, Taipei, Taiwan, Republic of China.

RB5. VALENCE BOND MODEL FOR $^1n\pi^*$ STATES OF 2,2',4,4'-TETRAMETHYLCYCLOBUTANE-1,3-DIONE(TMCBD)...15 min.(10:56)

W. R. WADT, Theoretical Division, Los Alamos National Laboratory, University of California, Los Alamos, New Mexico, 87545; W. R. MOOMAW, S. M. JAFFE, and JOHN W. THOMAN, JR., Thompson Chemical Laboratory, Williams College, Williamstown, Massachusetts, 01267.

RB6. THE CONVERGENCE PROPERTIES OF MR-CI ENERGIES..............................10 min.(11:13)

F. B. BROWN, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210; R. SHEPARD, Chemistry Division, Argonne National Laboratory, Argonne, Illinois, 60439; and I. SHAVITT, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.

RB7. THEORETICAL STUDY OF CS_2 POTENTIAL SURFACE.................................15 min.(11.25)

R. N. DIFFENDERFER and I. SHAVITT, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.

RB8. E5 will be presented here (E. YURTSEVER)..................................10 min.(11:42)

THURSDAY, JUNE 16, 1983 -- 8:30 A.M.

Room 1005, Physics Laboratory

Chairman: HOWARD STIDHAM, Department of Chemistry, University of Massachusetts, Amherst, Massachusetts.

RC1. A VIBRATIONAL CIRCULAR DICHROISM (VCD) STUDY OF THE STEREOCHEMISTRY OF Co(III) AND Cr(III) COMPLEXES..15 min.(8:30)

DARYL YOUNG, FAY RATNOWSKY, SUSAN BECKER, ELMER LIPP, and LAURENCE NAFIE, Department of Chemistry, Syracuse University, Syracuse, New York, 13210.

RC2. SOME TECHNICAL ASPECTS OF FTIR-VCD..15 min.(8:47)

E. D. LIPP and L. A. NAFIE, Department of Chemistry, Syracuse University, Syracuse, New York, 13210.

RC3. RAMAN OPTICAL ACTIVITY IN THE SKELETAL MOTIONS OF (+)-(3R)-METHYLCYCLOHEXANONE..15 min.(9:04)

T. B. FREEDMAN, C. G. ZIMBA, W. ZUK, and L. A. NAFIE, Department of Chemistry, Syracuse University, Syracuse, New York, 13210.

RC4. VIBRATIONAL CIRCULAR DICHROISM OF SMALL MOLECULES..15 min.(9:21)

A. ANNAMALAI and T. A. KEIDERLING, Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois, 60680.

RC5. COUPLED OSCILLATOR INTERPRETATION OF THE VCD OF DICARBONYL CONTAINING STEROIDS..15 min.(9:38)

USHA NARAYANAN and T. A. KEIDERLING, Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois, 60680.

Intermission

RC6. THE EFFECT OF DEUTERATION ON THE AMIDE I & II BANDS OF α-HELICAL POLYPEPTIDES AS EVIDENCED BY VCD STUDIES..15 min.(10:10)

A. C. SEN and T. A. KEIDERLING, Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois, 60680.

RC7. MAGNETIC VIBRATIONAL CIRCULAR DICHROISM OF METHYL HALIDES AND AMMONIA.......15 min.(10:27)

T. R. DEVINE and T. A. KEIDERLING, Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois, 60680.

RC8. SOME ASPECTS OF THE CIRCULAR DICHROISM MEASUREMENTS ON FOURIER TRANSFORM INFRARED (FTIR) SPECTROMETERS..15 min.(10:44)

D. F. MICHALSKA and P. L. POLAVARAPU, Department of Chemistry, Vanderbilt University, Nashville, Tennessee, 37235.

RC9. FOURIER TRANSFORM INFRARED ABSORPTION AND CIRCULAR DICHROISM OF CARBOHYDRATES..15 min.(11:01)

D. M. BACK and P. L. POLAVARAPU, Department of Chemistry, Vanderbilt University, Nashville, Tennessee, 37235.

RC10. SPECTROSCOPIC MODULATION TECHNIQUES TO OBSERVE INFRARED SPECTRA FOR SPECIES IN THE ELECTRODE SOLUTION INTERFACIAL REGION..15 min.(11:18)

J. W. RUSSELL, Department of Chemistry, Oakland University, Rochester, Michigan, 48063; A. BEWICK, Department of Chemistry, Southampton University, Southampton, Hampshire, England, SO9 5NH; and J. OVEREND, Department of Chemistry, University of Minnesota, Minneapolis, Minnesota, 55455.

RC11. INFRARED SPECTROSCOPY OF PHYSISORBED MOLECULES ON ALKALI HALIDE SURFACES....15 min.(11:35)

C. A. BAUMANN, W. C. SCHINZER, and G. E. EWING, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405.

RC12. TI4 will be presented here (B. GALABOV)..10 min.(11:52)

THURSDAY, JUNE 16, 1983 -- 1:30 P.M.

Room 1153, Physics Laboratory

Chairman Before Intermission: PAUL PARKER, Department of Physics, Michigan State University, East Lansing, Michigan.

Chairman After Intermission: G. GRANER, Laboratoire d'Infrarouge, Université de Paris-Sud, 91405 Orsay, France.

RE1. THEORY FOR VIBRATION-ROTATION-LARGE AMPLITUDE INTERNAL MOTION INTERACTIONS..15 min.(1:30)

C. RICHARD QUADE and YUHUA GUAN, Department of Physics, Texas Tech University, Lubbock, Texas, 79409.

RE2. THE INTERNAL COORDINATE FORMULATION OF THE VIBRATION-ROTATION ENERGIES FOR SYMMETRIC TOP AND SPHERICAL TOP MOLECULES..................................15 min.(1:47)

WILLIAM B. CLODIUS and C. RICHARD QUADE, Department of Physics, Texas Tech University, Lubbock, Texas, 79409.

RE3. HIGHER-ORDER ℓ-DOUBLING OF LINEAR MOLECULES................................15 min.(2:04)

JAMES K. G. WATSON, Herzberg Institute of Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A OR6, Canada.

RE4. HIGHER-ORDER VIBRATION-ROTATION CONSTANTS OF THE X_3 MOLECULE................15 min.(2:21)

JAMES K. G. WATSON, Herzberg Institute of Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A OR6, Canada.

RE5. SIMULATED ELECTRONIC SPECTRA OF HCN AND CNH OBTAINED WITH THE SEMIRIGID BENDER MODEL..10 min.(2:38)

S. C. ROSS and P. R. BUNKER, Herzberg Institute of Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A OR6, Canada and Department of Physics, Carleton University, Ottawa, Ontario, K1S 5B6, Canada.

RE6. SENSITIVITY OF QUASI-EQUILIBRIUM SEMIRIGID MODELS TO ISOTOPIC SUBSTITUTION..10 min.(2:50)

G. A. NATANSON, Department of Chemistry, The University of Chicago, Chicago, Illinois, 60637.

Intermission

RE7. THE NONRIGID BENDER HAMILTONIAN FOR A QUASILINEAR TRIATOMIC MOLECULE AND ITS APPLICATION TO CH_2..15 min.(3:15)

PER JENSEN and P. R. BUNKER, Herzberg Institute of Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A OR6, Canada.

RE8. HCNO AS A SEMIRIGID BENDER: THE DEGENERATE ν_4 STATE........................10 min.(3:32)

B. P. WINNEWISSER, Physikalisch-Chemisches Institut, Justus-Liebig-Universitaet Giessen, D-6300 Giessen, West Germany; and PER JENSEN, Herzberg Institute of Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A OR6, Canada.

RE9. CALCULATION AND INTERPRETATION OF THE VIBRATIONAL SPECTRA OF INTERACTING MOLECULES...15 min.(3:44)

STEVEN CHIN, Department of Chemistry, University of Florida, Gainesville, Florida, 32611; T. A. FORD, Department of Chemistry, University of Witwatersrand, Johannesburg, South Africa; and WILLIS B. PERSON, Department of Chemistry, University of Florida, Gainesville, Florida, 32611.

RE10. ON THE COLLISION DYNAMICAL ORIGINS OF PRESSURE BROADENING..................15 min.(4:01)

J. GELFAND, Applied Physics & Materials Laboratory, Department of Mechanical & Aerospace Engineering, Princeton University, Princeton, New Jersey, 08544; J. J. BELBRUNO, Department of Chemistry, Dartmouth College, Hanover, New Hampshire, 03755; K. VERGES, Applied Physics & Materials Laboratory, Department of Mechanical & Aerospace Engineering, Princeton University, Princeton, New Jersey, 08544; and H. RABITZ, Department of Chemistry, Princeton University, Princeton, New Jersey, 08544.

RE11. NITROGEN BROADENED HALFWIDTHS OF HF IN THE 1-0 BAND........................10 min.(4:18)

R. E. THOMPSON, Systems and Applied Sciences Corporation, Hampton, Virginia, 23666; J. H. PARK, M.A.H. SMITH, G. A. HARVEY, and J. M. RUSSELL, III, NASA Langley Research Center, Hampton, Virginia, 23665.

RE12. VIBRATIONAL SPECTRA FROM SEMI-CLASSICAL MECHANICS..........................15 min.(4:30)

D. M. WARDLAW, Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California, 91125; D. W. NOID, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 37830; and R. A. MARCUS, Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California, 91125.

RE13. ANHARMONICITY CONSTANTS IN ACETAMIDE AND THIOACETAMIDE.....................10 min.(4:47)

SIBSANKAR BALA, Department of Physics, University of Calcutta, 92, A.P.C. Road, Calcutta 700009, India; PRABHAT K. PANJA, Department of Chemistry, Presidency College, 86/1, College Street, Calcutta 700073, India; and PRADIP N. GHOSH, Department of Physics, University of Calcutta, 92, A.P.C. Road, Calcutta 700009, India.

RE14. VIBRATIONAL SPECTRUM AND NEARLY FREE INTERNAL ROTATION.....................10 min.(4:57)

SAJAL K. GANGULY and PRADIP N. GHOSH, Department of Physics, University of Calcutta, 92, A.P.C. Road, Calcutta 700009, India.

THURSDAY, JUNE 16, 1983 -- 1:30 P.M.

Room 1009, Physics Laboratory

Chairman Before Intermission: A. J. MERER, Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada.

Chairman After Intermission: J. L. HARDWICK, Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana.

RF1. HIGH RESOLUTION PHOTOELECTRON SPECTRUM OF THE $\tilde{B}$ (Π_1) STATE OF N_2O^+..........10 min. (1:30)

T. CVITAŠ, L. KLASINC, B. KOVAČ, The Rugjer Bošković Institute, Zagreb, Yugoslavia; R. MCDIARMID, National Institutes of Health, Bethesda, Maryland, 20205.

RF2. INVESTIGATION OF THE 550 nm REGION OF SUPERSONICALLY COOLED NO_2.............15 min. (1:42)

MENG-CHIH SU and DAVID L. MONTS, Department of Chemistry, University of Arkansas, Fayetteville, Arkansas, 72701.

RF3. SPIN PERTURBATIONS IN THE NO_2 VISIBLE SYSTEM...............................15 min. (1:59)

DAVID L. MONTS and MENG-CHIH SU, Department of Chemistry, University of Arkansas, Fayetteville, Arkansas, 72701.

RF4. COLLISIONAL TRANSFER OF ROTATIONAL ENERGY IN THE $^2B_1$ ELECTRONIC STATE OF NITROGEN DIOXIDE AND IMPROVED VIBRATIONAL AND ROTATIONAL CONSTANTS FOR THE (0,2,0) and (0,3,0) STATES..15 min. (2:16)

J. L. HARDWICK, Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana, 46556.

RF5. THE NEAR ULTRAVIOLET ABSORPTION SPECTRUM (Σ BANDS) OF $^{12}C^{34}S_2$...............15 min. (2:33)

J. L. HARDWICK, Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana, 46556; C. J. SELISKAR, and C. KINARD, Department of Chemistry, University of Cincinnati, Cincinnati, Ohio, 45221.

RF6. ROTATIONAL PERTURBATION AND ZEEMAN EFFECT IN THE $\tilde{A}^1A''-\tilde{X}^1A'$ TRANSITION OF HCF..10 min. (2:50)

T. SUZUKI, S. SAITO, and E. HIROTA, Institute for Molecular Science, Myodaiji, Okazaki 444, Japan.

Intermission

RF7 LASER EXCITATION SPECTRUM AND MICROWAVE OPTICAL DOUBLE RESONANCE SPECTRUM OF THE 3^1_0 BAND IN THE $\tilde{a}^3A_2-\tilde{X}^1A_1$ SYSTEM OF H_2CS..............................15 min. (3:15)

T. SUZUKI, S. SAITO, and E. HIROTA, Institute for Molecular Science, Myodaiji, Okazaki 444, Japan.

RF8. WHY IS FORMALDEHYDE NONPLANAR IN ITS $S_1(\pi^*,n)$ ELECTRONIC STATE?............15 min. (3:32)

K. K. INNES, Department of Chemistry, State University of New York, Binghamton, New York, 13901.

RF9. THE ELECTRIC DIPOLE MOMENT OF THE $\tilde{A}$ $^1A_2$ STATE OF FORMALDEHYDE BY STARK QUANTUM BEATS...15 min. (3:49)

MARTIN CARRERA, P. H. VACCARO, H.-L. DAI, and R. W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139.

RF10. ZERO FIELD AND ZEEMAN QUANTUM BEATS IN THE ACETYLENE $\tilde{A}$ ^1A_u STATE............15 min. (4:06)

M. LOMBARDI, Laboratoire de Spectrométrie Physique, Université Scientifique et Medicale de Grenoble, 38041 Grenoble, France; E. ABRAMSON, and R. W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139.

RF11. STIMULATED EMISSION SPECTROSCOPY OF H_2CO..................................15 min. (4:23)

H.-L. DAI, D. E. REISNER, P. H. VACCARO, C. KORPA, R. W. FIELD, and J. L. KINSEY, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139.

RF12. STIMULATED EMISSION SPECTROSCOPY OF ACETYLENE. STRUCTURE OF THE $\tilde{X}^1\Sigma_g^+$ STATE AT 28000 cm^{-1}..15 min. (4:40)

E. ABRAMSON, D. IMRE, J. L. KINSEY, and R. W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139.

RF13. Σ15 will be presented here (TERRY MILLER)..................................10 min. (4:57)

THURSDAY, JUNE 16, 1983 -- 1:30 P.M.

Room 1005, Physics Laboratory

Chairman Before Intermission: R. H. TIPPING, Optical Physics Division, U. S. Air Force Geophysics Laboratory, Hanscom Air Force Base, Massachusetts.

Chairman After Intermission: ALFONS WEBER, Molecular Spectroscopy Division, National Bureau of Standards, Washington, D.C.

RG1. ASYMMETRY OF THE INTERCOLLISIONAL DIP IN PRESSURE-INDUCED INFRARED SPECTRA..15 min.(1:30)

J. D. KELLEY and S. L. BRAGG, McDonnell Douglas Research Laboratories, Box 516, St. Louis, Missouri, 63166.

RG2. OBSERVATION OF THE $\Delta J = 5$ PURE ROTATIONAL TRANSITION IN SOLID HD............15 min.(1:47)

CHEN-HSIN LIEN, K. K. LO, J. R. GAINES, and K. NARAHARI RAO, Department of Physics, The Ohio State University, Columbus, Ohio, 43210.

RG3. HIGH RESOLUTION SPECTROSCOPY OF THE OVERTONE BANDS OF HD...................10 min.(2:04)

B. A. HARE, M. E. MICKELSON, Department of Physics, Denison University, Granville, Ohio, 43023; and J. T. TRAUGER, Division of Geological and Planetary Sciences and Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, 91125.

RG4. RAMAN SPECTROSCOPY OF HYDROGEN ISOTOPES: DETERMINATION OF EFFECTS OF CHANGES IN POLARIZABILITY ANISOTROPY ON INTENSITIES........................10 min.(2:16)

KIRK VEIRS, Los Alamos National Laboratory, Chemistry Division, Mail Stop C348, Los Alamos, New Mexico, 87544; and GERD M. ROSENBLATT, Los Alamos National Laboratory, Chemistry Division, Mail Stop J563, Los Alamos, New Mexico, 87544.

RG5. RAMAN SPECTRUM OF PYRIDINE RESONANT TO THE $S_2(\pi-\pi^*)$ STATE..................15 min.(2:28)

I. SUZUKA, College of Engineering, Nihon University, Koriyama, Fukushima-ken 963, Japan; Y. C. CHUNG, and G. E. LEROI, Department of Chemistry, Michigan State University, East Lansing, Michigan, 48824.

RG6. PRERESONANCE RAMAN EXCITATION PROFILES OF CAROTENOIDS......................15 min.(2:45)

C. M. PHILLIPS and G. E. LEROI, Department of Chemistry, Michigan State University, East Lansing, Michigan, 48824.

Intermission

RG7. AQUEOUS PYRIDINE BOROHYDRIDE-SILVER SOLS. I. DEPOLARIZATION RATIOS AND POLARIZATION DISPERSION..10 min.(3:15)

HOWARD D. STIDHAM and SCOTT M. HARRIS, Department of Chemistry, University of Massachusetts, Amherst, Massachusetts, 01003.

RG8. AQUEOUS PYRIDINE BOROHYDRIDE-SILVER SOLS. II. MULTIPLE SITE ADSORPTION....10 min.(3:27)

HOWARD D. STIDHAM and SCOTT M. HARRIS, Department of Chemistry, University of Massachusetts, Amherst, Massachusetts, 01003.

RG9. AQUEOUS PYRIDINE BOROHYDRIDE-SILVER SOLS. III. PYRAZINE AND PYRAZINE-d....10 min.(3:39)

HOWARD D. STIDHAM and ANDREA M. FEMINO, Department of Chemistry, University of Massachusetts, Amherst, Massachusetts, 01003.

RG10. INTENSITY SUM RULE FOR ITERATED VIRGULATE STRUCTURES........................10 min.(3:51)

HOWARD D. STIDHAM, Department of Chemistry, University of Massachusetts, Amherst, Massachusetts, 01003.

RG11. TIME RESOLVED RESONANCE RAMAN SPECTROSCOPY OF PHENOXYL RADICALS.............15 min.(4:03)

G.N.R. TRIPATHI and R. H. SCHULER, Radiation Laboratory and Department of Chemistry, University of Notre Dame, Notre Dame, Indiana, 46556.

RG12. CARS MEASUREMENTS IN TURBULENT FLAMES.....................................15 min.(4:20)

L. P. GOSS, Systems Research Laboratories, Incorporated, 2800 Indian Ripple Road, Dayton, Ohio, 45440

RG13. ULTRASENSITIVE COHERENT RAMAN SPECTROSCOPY OF THIN FILMS AND SURFACES.......15 min.(4:37)

W. M. HETHERINGTON, Department of Chemistry, University of Arizona, Tucson, Arizona, 85721; G. I. STEGEMAN, R. M. FORTENBERRY, Optical Sciences Center, University of Arizona, Tucson, Arizona, 85721; and N. E. VAN WYCK, Department of Chemistry, University of Arizona, Tucson, Arizona, 85721.

RG14. F14 will be presented here (E. J. HEILWEIL)...............................10 min.(4:52)

THURSDAY, JUNE 16, 1983 -- 1:30 P.M.

Room 1008, Evans Chemical Laboratory

Chairman: V. F. KALASINSKY, Department of Chemistry, Mississippi State University, Mississippi State, Mississippi.

RH1. INFRARED SPECTRA OF MATRIX ISOLATED HYDROGEN FLUORIDE AND VIBRATIONAL PREDISSOCIATION OF THE DIMER....15 min.(1:30)

R. L. REDINGTON and D. F. HAMILL, Department of Chemistry, Texas Tech University, Lubbock, Texas, 79409.

RH2. MATRIX ISOLATION STUDY OF SO_2·AMINE COMPLEXES....15 min.(1:47)

CRAIG S. SASS and BRUCE S. AULT, Department of Chemistry, University of Cincinnati, Cincinnati, Ohio, 45221.

RH3. INFRARED MATRIX ISOLATION STUDIES OF REACTIVE OXYANIONS....15 min.(2:04)

SHELLE J. DAVID and BRUCE S. AULT, Department of Chemistry, University of Cincinnati, Cincinnati, Ohio, 45221.

RH4. MATRIX ISOLATION VIBRATIONAL SPECTRA OF METAL COORDINATED OXYANIONS. THE USE OF ISOTOPE PATTERNS AND BAND INTENSITIES IN STRUCTURAL CHARACTERIZATION OF HIGH TEMPERATURE MOLECULES....15 min.(2:21)

L. BENCIVENNI, Laboratorio Di Spettroscopia Molecolare Del Centro Di Termodinamica Chimica Alte Temperature(CNR), Istituto Di Chimica Fisica, Università Di Roma, 00185 Roma, Italy; K. A. GINGERICH, and H. M. NAGARATHNA, Department of Chemistry, Texas A&M University, College Station, Texas, 77843.

RH5. INFRARED SPECTRA OF THE MATRIX-ISOLATED CHLORIDES OF IRON, COBALT, AND NICKEL....15 min.(2:38)

D. W. GREEN, Chemical Technology Division, Argonne National Laboratory, Argonne, Illinois, 60439; D. P. MCDERMOTT, Department of Chemistry, Lafayette College, Easton, Pennsylvania, 18042; and A. BERGMAN, Department of Chemistry, Brown University, Providence, Rhode Island, 02912.

Intermission

RH6. VIBRATIONAL SPECTRUM OF THE NITROMETHYL FREE RADICAL TRAPPED IN SOLID ARGON....15 min.(3:10)

MARILYN E. JACOX, Molecular Spectroscopy Division, National Bureau of Standards, Washington, D.C., 20234.

RH7. LIGHT-INDUCED PREPARATION AND ISOMERIZATION OF UNSTABLE SPECIES IN LOW-TEMPERATURE MATRICES....15 min.(3:27)

R. P. MÜLLER and J. ROBERT HUBER, Physikalisch-Chemisches Institut der Universität Zürich, CH-8057 Zürich, Switzerland.

RH8. FLUORESCENCE STUDIES OF MATRIX ISOLATED TRANSITION METAL ATOMS COMPLEXED WITH SMALL UNSATURATED MOLECULES....15 min.(3:44)

R. RUBINOVITZ and E. R. NIXON, Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania, 19104.

RH9. MATRIX ISOLATION STUDIES OF NUCLEIC ACID CONSTITUENTS. I. INFRARED SPECTRA OF URACIL MONOMERS....15 min.(4:01)

M. SZCZESNIAK, M. J. NOWAK, H. ROSTKOWSKA, K. SZCZEPANIAK, Institute of Physics, Polish Academy of Sciences, 02-668 Warsaw, Poland; W. B. PERSON, Department of Chemistry, University of Florida, Gainesville, Florida, 32611; and D. SHUGAR, Institute of Biochemistry and Biophysics, Polish Academy of Sciences, 02-532 Warsaw, Poland.

RH10. Σ2 will be presented here(D. J. DIESTLER)....15 min.(4:18)

RH11. Σ9 will be presented here(JACK G. KAY)....15 min.(4:35)

FRIDAY, JUNE 17, 1983 -- 8:30 A.M.

Room 1153, Physics Laboratory

Chairman: P. N. GHOSH, Department of Physics, University of Calcutta, Calcutta - 700009, India.

FA1. FITTING OF VIBRATION ROTATION SPECTRA OF H_2S AND H_2Se ....15 min.(8:30)

WM. C. LANE and T. H. EDWARDS, Department of Physics and Astronomy, Michigan State University, East Lansing, Michigan, 48824.

FA2. THE PURE ROTATION SPECTRUM OF HYDROGEN SULFIDE ....10 min.(8:47)

C. CAMY-PEYRET, J.-M. FLAUD, Laboratoire de Physique Moléculaire et d'Optique Atmosphérique, CNRS, Campus d'Orsay, 91405, Orsay, France; and J.W.C. JOHNS, Herzberg Institute of Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A 0R6, Canada.

FA3. HIGH RESOLUTION SPECTRUM OF THE FUNDAMENTAL ν_2 OF DNCO ....10 min.(8:59)

D. A. STEINER, Department of Physics, The Pennsylvania State University, University Park, Pennsylvania, 16802; K. WISHAH, Department of Physics, University of Jordan, Faculty of Science, Amman, Jordan; S. R. POLO, Department of Physics, The Pennsylvania State University, University Park, Pennsylvania, 16802; and T. K. McCUBBIN, JR., (on sabbatical) Laboratoire de Spectronomie Moléculaire, Université Pierre et Marie Curie, 4 Place Jussieu, 75005 Paris, France.

FA4. ANALYSIS OF THE ν_2, ν_5 AND $\nu_3+\nu_6$ BANDS OF CHF_3 IN THE 8-9 MICRON REGION....15 min.(9:11)

G. GRANER and G. GUELACHVILI, Laboratoire d'Infrarouge, Université de Paris-Sud, 91405 Orsay, France.

FA5. THE DIODE LASER HETERODYNE OF CDF_3 ....10 min.(9:28)

JOSEPH P. SATTLER, RICHARD P. LEAVITT, and TERRANCE L. WORCHESKY, U. S. Army Electronics Research and Development Command, Harry Diamond Laboratories, 2800 Powder Mill Road, Adelphi, Maryland, 20783.

FA6. ANALYSIS OF THE ν_6 BAND OF CHD_2F ....15 min.(9:40)

D. F. EGGERS, Department of Chemistry, University of Washington, Seattle, Washington, 98195; and J.W.C. JOHNS, Herzberg Institute of Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A 0R6, Canada.

Intermission

FA7. ANALYSIS OF ALLENE-D_4 BANDS IN THE 4.2 - 5.3 μm REGION......................15 min.(10:10)

J. PLIVA, Department of Physics, The Pennsylvania State University, University Park, Pennsylvania, 16802; K. ROUSAN, Department of Physics, Yarmouk University, Irbid, Jordan; and S. R. POLO, Department of Physics, The Pennsylvania State University, University Park, Pennsylvania, 16802.

FA8. INTENSITY AND BROADENING STUDIES OF PROPANE, ACETYLENE, METHYL CHLORIDE AND ETHANE IN THE 12-14 μm REGION ....10 min.(10:27)

W. E. BLASS, J. K. LAWSON, G. W. HALSEY, and M. A. DAKHIL, Molecular Spectroscopy Laboratory, Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee, 37996.

FA9. DETAILED ANALYSIS OF THE 5 μm ABSORPTION REGION OF $^{13}CD_3F$ ....15 min.(10:39)

G. W. HALSEY, M. A. DAKHIL, and W. E. BLASS, Molecular Spectroscopy Laboratory, Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee, 37996.

FA10. ANALYSIS OF $2\nu_2$ BAND OF $^{12}CD_3F$ ....10 min.(10:56)

M. A. DAKHIL, G. W. HALSEY, and W. E. BLASS, Molecular Spectroscopy Laboratory, Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee, 37996.

FA11. THE HIGH RESOLUTION SPECTROSCOPY OF CYCLOPROPANE $\nu_9+\nu_{10}$ COMBINATION BAND PERTURBED BY FERMI AND CORIOLIS RESONANCES..........................15 min.(11:08)

ZHU QINGSHI, Salt Lake Institute of Chinese Academy of Sciences, Sining, Qinghai, People's Republic of China; SHEN ZHIYE, SHEN HUIHUA, LIU HUIFANG, ZHANG BAOSHU, HUANG RUNLAN, and ZHANG CUNHAO, Dalian Institute of Chemical Physics, Dalian, People's Republic of China.

FA12. VISIBLE AND NEAR INFRARED SPECTRA OF CYCLOPROPANE..........................10 min.(11:25)

S. L. BRAGG, McDonnell Douglas Research Laboratories, P.O. Box 516, St. Louis, Missouri, 63166.

FA13. FIRST OBSERVATION OF $^{12}C_2H_4$ AND $^{12}C^{13}CH_4$ HOT BANDS IN THE 10 μm REGION......15 min.(11:37)

L. HENRY, A. VALENTIN, Laboratoire de Spectronomie Moléculaire, Université Pierre et Marie Curie, F-75230 Paris, France; M. DE VLEESCHOUWER, Ch. LAMBEAU, and A. FAYT, Department of Molecular Spectroscopy, University of Louvain, Chemin du Cyclotron, 2, B-1348 Louvain-La-Neuve, Belgium.

FA14. HIGH VIBRATIONAL OVERTONES IN $SiHCl_3$ AND SiH_2Cl_2..........................10 min.(11:54)

R. A. BERNHEIM, F. W. LAMPE, J. F. O'KEEFE, and J. R. QUALEY, III, Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania, 16802.

FA15. MOLECULAR CONSTANTS OF SEVERAL LEVELS OF ISOTOPIC CARBON DISULFIDE FROM IR SPECTRA.. 5 min.(12:06)

ROMOLA D'CUNHA, JON MANHEIM, K. NARAHARI RAO, Department of Physics, The Ohio State University, Columbus, Ohio, 43210; and C. J. SELISKAR, Department of Chemistry, University of Cincinnati, Cincinnati, Ohio, 45221. Permanent address of JON MANHEIM: Wright Patterson Air Force Base, Ohio, 45433.

FA16. Π10 will be presented here (H. A. FRY)....................................10 min.(12:11)

FRIDAY, JUNE 17, 1983 -- 8:30 A.M.

Room 1009, Physics Laboratory

Chairman: D. L. HUESTIS, Molecular Physics Laboratory, Stanford Research Institute International, Menlo Park, California.

FB1. "BEST" SPECTROSCOPIC CONSTANTS FOR HgBr FROM DIRECT FITS OF MULTIPLE BAND SYSTEMS TO POLYNOMIALS AND NEAR-DISSOCIATION EXPANSIONS................15 min.(8:30)

J. GAIL ASHMORE and JOEL TELLINGHUISEN, Department of Chemistry, Vanderbilt University, Nashville, Tennessee, 37235.

FB2. INTERFACING A MICRODENSITOMETER TO A MICROCOMPUTER..........................15 min.(8:47)

O. CARLYSLE SALTER and JOEL TELLINGHUISEN, Department of Chemistry, Vanderbilt University, Nashville, Tennessee, 37235.

FB3. REFLECTION AND INTERFERENCE STRUCTURE IN DIATOMIC FRANCK-CONDON DISTRIBUTIONS...15 min.(9:04)

JOEL TELLINGHUISEN, Department of Chemistry, Vanderbilt University, Nashville, Tennessee, 37235.

FB4. THE 2880-Å EMISSION SPECTRUM OF I_2: ION-PAIR STATES NEAR 47 000 CM^{-1}.......15 min.(9:21)

K. S. VISWANATHAN and JOEL TELLINGHUISEN, Department of Chemistry, Vanderbilt University, Nashville, Tennessee, 37235.

FB5. CYBERNETIC REANALYSIS OF THE S_2 $B^3\Sigma_u^- - X^3\Sigma_g^-$ TRANSITION........................15 min.(9:33)

GEORGE VINANSKY and ALLAN L. SMITH, Department of Chemistry, Drexel University, Philadelphia, Pennsylvania, 19104.

Intermission

FB6. VARIATION OF THE ELECTRONIC TRANSITION MOMENT IN THE A $^2\Pi$ - X $^2\Pi$ SYSTEM OF CℓO...15 min.(10:05)

S. A. BARTON, J. A. COXON, and U. K. ROYCHOWDHURY, Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, B3H 4J3, Canada. *Present address of S. A. BARTON: DRE Valcartier,* P.O. Box 880, Courcelette, Quebec, GOA 1RO, Canada.

FB7. ROTATIONAL ANALYSIS OF THE A $^2\Pi$ → X $^2\Pi$ SYSTEM OF THE SULPHUR MONOXIDE CATION...15 min.(10:22)

J. A. COXON and S. C. FOSTER, Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, B3H 4J3, Canada. Present address of S. C. FOSTER: Herzberg Institute of Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A OR6, Canada.

FB8. ROTATIONAL ANALYSIS OF THE B $^2\Sigma^+$ → X $^2\Sigma^+$ SYSTEM OF AℓO.....................10 min.(10:39)

J. A. COXON and S. NAKAKIS, Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, B3H 4J3, Canada.

FB9. POPULATION ANOMALIES IN AN Mg + N_2O FLAME.................................15 min.(10:57)

P.C.F. IP, JEFFREY A. GRAY, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139; K. CROSS, 32 Chadwick Street, Hilton Park, Western Australia 6163; and R. W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139.

FB10. THE CaO $c^3\Sigma^+$ - $a^3\Pi_i$ SYSTEM..15 min.(11:08)

J. B. NORMAN, Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139; K. J. CROSS, 32 Chadwick Street, Western Australia 6163; H. S. SCHWEDA, Fakultat fur Physik Universitat Bielefeld, 4800 Bielefeld 1, West Germany; R. F. BARROW, Physical Chemistry Laboratory, Oxford University, Oxford, England, OX1 3QZ; and R. W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139.

FB11. CW ION LASER EXCITATION OF OH AND NH IN AN ATMOSPHERIC PRESSURE FLAME.......10 min.(11:25)

J. A. VANDERHOFF, A. J. KOTLAR, and W. R. ANDERSON, Ballistic Research Laboratory, DRDAR-BLI, Aberdeen Proving Ground, Maryland, 21078.

FB12. SPECTROSCOPY OF THE $He^*(2^3S)$-C_2H_2 FLAME....................................15 min.(11:37)

D. H. WINICUR, J. L. HARDWICK, and S. N. MURPHY, Department of Chemistry and Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana, 46556.

FB13. HIGH RESOLUTION LASER SPECTRUM OF THE SECOND POSITIVE BAND SYSTEM OF N_2 UNDER ELECTRON BEAM EXCITATION..10 min.(11:54)

PUTCHA VENKATESWARLU and S. K. BASU, Department of Physics, Alabama Agricultural and Mechanical University, Normal, Alabama, 35762, Herzberg Institute of Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A 0R6, Canada, and Department of Physics, Indian Institute of Technology, Kanpur, India, 208016.

FRIDAY, JUNE 17, 1983 -- 8:30 A.M.

Room 1005, Physics Laboratory

Chairman: JOHN PARSON, Department of Chemistry, The Ohio State University, Columbus, Ohio.

FC1. STRUCTURE OF LiNC BY MOLECULAR BEAM ELECTRIC RESONANCE SPECTROSCOPY.........15 min.(8:30)

J. J. VAN VAALS, W. LEO MEERTS, and A. DYMANUS, Afd. Atoom-en Molekuulfysica, Katholieke Universiteit Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

FC2. ROTATIONAL-VIBRATIONAL STATE DEPENDENCE OF NUCLEAR QUADRUPOLE INTERACTIONS IN DIATOMIC MOLECULES..10 min.(8:47)

JAMES CEDERBERG and DAVID NITZ, St. Olaf College, Northfield, Minnesota, 55057.

FC3. HYPERFINE SPECTRUM OF KCℓ AS OBSERVED BY MOLECULAR BEAM ELECTRIC RESONANCE SPECTROSCOPY..10 min.(8:59)

DAVID NITZ, JAMES CEDERBERG, KEITH HETZLER, ARTHUR KOTZ, and STANLEY TEAD, St. Olaf College, Northfield, Minnesota, 55057.

FC4. VIBRATIONAL RELAXATION OF LINEAR MOLECULES IN SUPERSONIC EXPANSIONS.........15 min.(9:11)

R. L. DELEON and J. S. MUENTER, Department of Chemistry, University of Rochester, Rochester, New York, 14627.

FC5. MBER SPECTROSCOPY OF IR LASER EXCITED VIBRATIONAL STATES....................10 min.(9:28)

WILLIAM EBENSTEIN and J. S. MUENTER, Department of Chemistry, University of Rochester, Rochester, New York, 14627.

FC6. DIPOLE MOMENTS OF EXCITED VIBRATIONAL STATES OF HCN.........................15 min.(9:40)

R. L. DELEON and J. S. MUENTER, Department of Chemistry, University of Rochester, Rochester, New York, 14627.

Intermission

FC7. ROTATIONAL SPECTRA AND STRUCTURES OF H_2O-CO_2, HDO-CO_2 AND D_2O-CO_2..........15 min.(10:10)

K. I. PETERSON, T. A. FISHER, and W. KLEMPERER, Department of Chemistry, Harvard University, Cambridge, Massachusetts, 02138.

FC8. THE MYSTERY OF ArHCN...15 min.(10:27)

G. T. FRASER, K. R. LEOPOLD, F. J. LIN, and W. KLEMPERER, Department of Chemistry, Harvard University, Cambridge, Massachusetts, 02138.

FC9. ROTATIONAL SPECTRA AND STRUCTURES OF HCN-CO_2 AND DCN-CO_2....................15 min.(10:44)

K. R. LEOPOLD, G. T. FRASER, and W. KLEMPERER, Department of Chemistry, Harvard University, Cambridge, Massachusetts, 02138.

FC10. DEUTERIUM QUADRUPOLE COUPLING CONSTANTS IN VIBRATIONALLY EXCITED HCCD: EVIDENCE FOR ELECTRON REORGANIZATION......................................15 min.(11:01)

M. D. MARSHALL and W. KLEMPERER, Department of Chemistry, Harvard University, Cambridge, Massachusetts, 02138.

FC11. Σ12 will be presented here(J. A. SHEA)....................................10 min.(11:18)

FC12. Σ13 will be presented here(J. A. SHEA)...................................15 min.(11:30)

Σ SESSION

LATE PAPERS: THE SESSIONS IN WHICH THEY ARE SCHEDULED APPEAR IN PARENTHESES FOLLOWING THE TIMES REQUIRED FOR PRESENTATION.

Σ1. MICROWAVE SPECTRA AND STRUCTURE OF METHYLGERMYL CYANIDE....................10 min.(TG9)

A. B. MOHAMAD and J. R. DURIG, Department of Chemistry, University of South Carolina, Columbia, South Carolina, 29208.

Σ2. THEORETICAL ANALYSIS OF INFRARED ABSORPTION LINESHAPES OF HCl ISOLATED IN AN ARGON MATRIX..15 min.(RH10)

D. J. DIESTLER, Department of Chemistry, Purdue University, West Lafayette, Indiana, 47907.

Σ3. ZEEMAN SPLITTING OF THE PHOSPHORESCENCE OF PALLADIUM-PHTHALOCYANINE IN A SHPOLSKI'I MATRIX..10 min.(TH'5)

W.-H. CHEN, K. E. RIECKHOFF, and E.-V. VOIGT, Departments of Chemistry and Physics, Simon Fraser University, Burnaby, British Columbia, V5A 1S6, Canada.

Σ4. THE EFFECT OF PRESSURE ON MOLECULAR RYDBERG TRANSITIONS....................15 min.(TH'6)

J. L. ADOLPH, D. L. BESTWICK, and J. D. SCOTT, Department of Chemistry, University of Montana, Missoula, Montana, 59812.

Σ5. STURMIAN BASIS MATRIX SOLUTION OF VIBRATIONAL POTENTIALS...................10 min.(RB8)

E. YURTSEVER, Orta Dogu Teknik Üniversitesi, Kimya Bölümü, Ankara-Turkey.

Σ6. OPTICAL STARK EFFECTS IN THE STIMULATED RAMAN SPECTRUM OF O_2................10 min.(WG 7)

R. A. HILL, A. OWYOUNG, and P. ESHERICK, Sandia National Laboratories, Division 2562, Albuquerque, New Mexico, 87185.

Σ7. HIGH RESOLUTION FOURIER TRANSFORM SPECTRA OF THE ν_1 BAND OF HYDRAZOIC ACID (HN_3)..10 min.(ME15)

A. S-C. CHEUNG and A. J. MERER, Department of Chemistry, University of British Columbia, Vancouver, British Columbia, V6T 1Y6, Canada.

Σ8. FOURIER TRANSFORM INFRA-RED SPECTRUM OF CrO NEAR 8000 CM^{-1}.................15 min.(TB10)

A. S-C. CHEUNG, A. J. MERER, and W. ŻYRNICKI, Department of Chemistry, University of British Columbia, Vancouver, British Columbia, V6T 1Y6, Canada. Permanent address of W. ŻYRNICKI: Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Technical University of Wroclaw, 50-370 Wroclaw, Poland.

Σ9. MATRIX ISOLATION AND FTIR SPECTROSCOPIC STUDIES OF RuO, RuO_2, RuO_3 and RuO_4...15 min.(RH11)

DAVID W. GREEN, Chemical Technology Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois, 60439; JACK G. KAY, Department of Chemistry, Drexel University, Philadelphia, Pennsylvania, 19104; GERALD T. REEDY, Chemical Technology Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois, 60439; and GEORGE L. ZIMMERMAN, Department of Chemistry, Bryn Mawr College, Bryn Mawr, Pennsylvania, 19010.

Σ10. DOPPLER SHIFT AND ION MOBILITY MEASUREMENTS OF ArH^+ IN A He DC GLOW DISCHARGE BY DIODE LASER SPECTROSCOPY......................................10 min.(MF13)

NATHAN N. HAESE, FU-SHIH PAN, and TAKESHI OKA, Department of Chemistry, University of Chicago, Chicago, Illinois, 60637.

Σ11. SUB-DOPPLER SATURATION SPECTROSCOPY USING MICROWAVE SIDEBANDS ON CO_2 LASER LINES: HYPERFINE STRUCTURE IN NH_3 AND VIBRATION-INDUCED DIPOLE MOMENT IN TETRAHEDRAL MOLECULES....................................15 min.(RA7)

GOTTFRIED MAGERL, JOAN M. FRYE, WELF A. KREINER, and TAKESHI OKA, Department of Chemistry, University of Chicago, Chicago, Illinois, 60637.

Σ12. THE ROTATIONAL ZEEMAN EFFECT IN THE ArOCS VAN DER WAALS COMPLEX............10 min.(FC11)

J. A. SHEA, W. G. READ, and E. J. CAMPBELL, School of Chemical Sciences, University of Illinois, Urbana, Illinois, 61801.

Σ 13. THE ROTATIONAL ZEEMAN EFFECT IN THE OCS-HF, OCO-DF, OCO-HCℓ AND SCO-HF COMPLEXES..........15 min.(FC12)

J. A. SHEA, W. G. READ, and E. J. CAMPBELL, School of Chemical Sciences, University of Illinois, Urbana, Illinois, 61801

Σ 14. LASER INDUCED FLUORESCENCE SPECTRA OF FREE-JET COOLED ORGANIC FREE RADICALS - VINOXY, CYCLOPENTADIENYL, AND BENZYL..........15 min.(TF11)

M. C. HEAVEN, Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois, 60616; TERRY A. MILLER, and L. DIMAURO, Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey, 07974.

Σ 15. LASER INDUCED FLUORESCENCE SPECTROSCOPY OF MOLECULAR IONS AND IONIC CLUSTERS..........10 min.(RH11)

TERRY MILLER, L. DIMAURO, Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey, 07974; M. C. HEAVEN, Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois, 60616; and V. E. BONDEBEY, Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey, 07974.

[illegible] SESSION

PAPERS RECEIVED AFTER THE PROGRAM WAS PRINTED ARE LISTED BELOW:

1. LASER SPECTROSCOPY OF THE $^{1}A''-X^{1}A'$ SYSTEM OF CuOH AND CuOD....................15 min.(TB11)

MITCHELL TRKULA and DAVID O. HARRIS, Department of Chemistry and Quantum Institute, University of California, Santa Barbara, California, 93106.

2. DIRECT OBSERVATION OF $^{3}\Sigma_{g}$ STATES OF THE Na_2 MOLECULE BY OPTICAL-OPTICAL DOUBLE RESONANCE...10 min.(TF12)

LI LI and ROBERT W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139. Permanent address of LI LI: Qinghai Institute of Salt Lake, Academia Sinica, Xining, China.

3. SINGLE CRYSTAL RAMAN SPECTRA OF MAGNESIUM AND ZINC PERCHLORATE HEXAHYDRATES...15 min.(FD1)

M. B. PATEL, ANSHU AGARWAL, and H. D. BIST, Department of Physics, Indian Institute of Technology, Kanpur 208 016, India.

4. BOND POLAR PARAMETERS FROM INTEGRATED INFRARED INTENSITIES....................15 min.(RC12)

B. GALABOV, Department of Chemistry, University of Sofia, 1126, Sofia, Bulgaria.

5. INFRARED AND RAMAN SPECTRA OF MATRIX ISOLATED $(PbO)_n$ SPECIES..................15 min.(FD2)

Y. J. PARK, R. K. KHANNA, Department of Chemistry, University of Maryland, College Park, Maryland, 20742; and BERTRAM DONN, Goddard Space Flight Center, Greenbelt, Maryland, 20771.

6. VIBRATIONAL SPECTROSCOPIC STUDIES OF SO_3 IN SOLID STATE.......................15 min.(FD3)

G. V. JERE, R. K. KHANNA, Department of Chemistry, University of Maryland, College Park, Maryland, 20742; and M. OSPINA and J. PEARL, Goddard Space Flight Center, Greenbelt, Maryland, 20771

7. RESONANCE RAMAN STUDIES OF GAS PHASE AND CONDENSED PHASE METALLO-PORPHYRINS: TEMPERATURE DEPENDENCE OF VIBRATIONAL FREQUENCIES AND VIBRATIONAL ANHARMONICITIES...20 min.(FD4)

J. L. MURTAUGH and S. A. ASHER, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, 15260.

8. DEVELOPMENT OF INSTRUMENTATION FOR TUNABLE UV RESONANCE RAMAN STUDIES IN THE 217-400 NM SPECTRAL region...15 min.(FD5)

S. A. ASHER, C. R. JOHNSON, and J. L. MURTAUGH, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, 15260.

9. UV RESONANCE RAMAN EXCITATION PROFILES OF BENZENE IN THE 217 TO 270 NM SPECTRAL REGION..20 min.(FD6)

C. R. JOHNSON and S. A. ASHER, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, 15260.

10. OBSERVATION AND ANALYSIS OF THE FUNDAMENTAL BENDING MODE OF T_2O..............10 min.(FA16)

H. A. FRY, L. H. JONES, and J. E. BAREFIELD, Los Alamos National Laboratory, Los Alamos, New Mexico, 87545.

11. OBSERVATION OF VISIBLE ABSORPTION IN THE FOURTH OVERTONE OF THE OH STRETCH IN GASEOUS CH_3OH...15 min.(TG10)

G. O. BRINK, Department of Physics and Astronomy, State University of New York at Buffalo, Amherst, New York, 14260

Π12. MAGNETIC ROTATION SPECTROSCOPY OF SINGLET METHYLENE............................15 min.(TB12)

H. PETEK, D. J. NESBITT, and C. BRADLEY MOORE, Department of Chemistry, University of California, Berkeley, Berkeley, California, 94720.

Π13. DIRECT OBSERVATION OF INTRAMOLECULAR ENERGY REDISTRIBUTION IN p-DIFLUOROBENZENE BY PICOSECOND GATING..10 min.(WH9)

R. MOORE, F. E. DOANY, E. J. HEILWEIL, and R. M. HOCHSTRASSER, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania, 19104.

Π14. TRANSIENT GRATING SPECTROSCOPY USING THE PHASE CONJUGATE CONFIGURATION........10 min.(RG14)

E. J. HEILWEIL and R. M. HOCHSTRASSER, Department of Chemistry and Laboratory for the Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania, 19104.

SESSION FD WILL BE HELD IN ROOM 1008 EVANS CHEMICAL LABORATORY STARTING AT 8:30 A.M., FRIDAY, JUNE 17.

The chairman will be: W. M. HETHERINGTON, Department of Chemistry, University of Arizona, Tucson, Arizona.

The following papers will be presented in this session: Π3, Π5, Π6, Π7, Π8, Π9

ME1. (1:30)

MEASUREMENTS OF VARIOUS ISOTOPIC RATIOS AT THE 0.1 PERCENT PRECISION LEVEL WITH A COMPUTER CONTROLLED DIODE LASER SPECTROMETER SYSTEM

R. L. SAMS AND J. R. DEVOE

A computer controlled diode laser system has been designed and built which is capable of measuring relative intensities of absorption lines to a high degree of precision in a number of light atmospheric trace gases. Measurements of the relative $^{13}C/^{12}C$ ratios in a series of CO_2 samples will be presented. It will be shown that a relative accuracy of 0.1 percent can be obtained with a sample size of about 500 picograms of $^{13}CO_2$. The ratio of $^{18}O/^{16}O$ was measured at the same time with comparable accuracy. A discussion of the experimental design and measurement capabilities will be given.

Address of Sams and DeVoe: National Bureau of Standards, Center for Analytical Chemistry, Laser Analytical Chemistry Group, Washington D. C., 20234.

ME2. (1:47)

LINE INTENSITY MEASUREMENTS OF ISOTOPIC, HOT BAND, AND HOT HOT BAND TRANSITIONS IN THE ν_2 REGION OF CARBON DIOXIDE

J. O'CONNELL, A. W. MANTZ, W. O. GALLERY, S. A. CLOUGH

Room temperature intensity measurements of individual lines for $^{12}C^{16}O_2$ ($10^00 - 01^10$) and ($03^30 - 02^20$) as well as $^{12}C^{16}O^{17}O$ ($01^10 - 00^00$) transitions have been completed using a lead salt tunable diode laser system. Line intensities are reproduced to better than 6% (3σ) under completely independent experimental conditions. In these experiments absorption pathlengths are varied from 2 cm to 100m as appropriate, and intensity measurements are conducted on samples with total pressures between 0.01 Torr and 6 Torr.

Intensities reported here for $^{12}C^{16}O^{17}O$ and for hot band transitions of the major isotope differ significantly from those previously reported.

We will describe the experiments and our results in this paper.

Address of Gallery and Clough: AFGL/OPI, Hanscom AFB, MA 01731
Address of O'Connell and Mantz: Laser Analytics, Inc., 25 Wiggins Ave., Bedford, MA 01730

This work was sponsored by AFGL contract No. F19628-80-C-0181.

ME3. (1:59)

WING CORRECTIONS TO MEASURED HALF-WIDTHS

BERNARD FRIDOVICH

A simple method is presented for correcting line half-widths, measured from high resolution data, for errors introduced by the uncertainty in locating the 100% transmittance line. The correction is calculated from the initial measurement of: central transmittance $\tau(0)$; line half-width at $\sqrt{\tau(0)}$; and the distance from line center to the intersection of $\tau(\nu)$ and the 100% line g. By assuming a line shape-Lorentz or Voigt - we can compute a correction.

Address: NOAA/NESDIS, FOB #4, E/RA21, Washington, D.C. 20233

ME4. (2:16)

STRENGTHS, HALF-WIDTHS, AND TEMPERATURE DEPENDENCE OF HALF-WIDTH, FOR R BRANCH SPECTRAL LINES IN THE ν_3 AND $(\nu_2+\nu_3)-\nu_2$ BANDS OF CO_2 NEAR 4.3 μm, MEASURED WITH A DIODE LASER

V. MALATHY DEVI, B. FRIDOVICH, D.J. JONES, AND D.G.S. SNYDER

Absolute line strengths have been measured, at room temperature, for R branch spectral lines of the ν_3 bands of $^{12}C^{16}O^{18}O$ and $^{12}C^{16}O^{17}O$, and for the $(\nu_2+\nu_3)-\nu_2$, and $(\nu_1+\nu_3)-\nu_1$ bands of $^{12}C^{16}O_2$, in the 2365-2393 cm^{-1} spectral region using a tunable diode laser. Self- and nitrogen-broadened half-widths were measured for some of the ν_3 lines of $^{12}C^{16}O_2$ and $^{12}C^{16}O^{17}O$. Nitrogen-broadened half-widths were measured for the $(\nu_2+\nu_3)-\nu_2$ lines of $^{12}C^{16}O_2$. From half-width measurements made on nitrogen-broadened lines over a temperature range from 217 to 299K we have calculated the temperature coefficient of the Lorentz half-width n, defined as $b_L^o(T) = b_L^o(T_o)\ (T/T_o)^{-n}$, for the ν_3 and $(\nu_2+\nu_3)-\nu_2$ bands of $^{12}C^{16}O_2$. The mean values of the n are 0.757 ± 0.008 and 0.789 ± 0.015, respectively. The band strengths deduced from line strengths for both the ν_3 and $(\nu_2+\nu_3)-\nu_2$ bands of $^{12}C^{16}O_2$ are about 5% lower than those of the latest AFCL line listing. Isotopic band strengths for the ν_3 bands are also reported.

Address: NOAA/NESDIS, FOB #4, E/RA21, Washington, D.C. 20233

ME5. (2:28)

FOREIGN GAS BROADENED WIDTHS OF CO_2 AT 9.4 AND 10.4μm

M. HOKE, B. HAWKINS, AND J. SHAW

The pressure broadened widths of lines of carbon dioxide broadened by oxygen and dry air have been estimated by an analysis of the 9.4 and 10.4μm bands using methods described previously[1]. The data were obtained with a commercial Nicolet F.T.S. of resolution approximately 0.06 cm^{-1}, a path length of 130 meters, and pressures of approximately one atmosphere. Spectra were obtained over a temperature range of about 60°C, including room temperature.

Preliminary estimates for O_2 broadening are consistent with the few previous results[2,3]. In particular it has been found that the temperature dependence $(T_o/T)^\gamma$ is more satisfactorily modeled with an exponent γ of approximately .75.

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1 M. Hoke and J. Shaw, Applied Optics, 22, 328 (1983).

2 M. O. Bulanin, V. P. Bulychev, and E. B. Khodos, Opt. Spectrosc., 48(4), 403 (1980).

3 R. L. Abrams, Applied Physics Letters, 25, 609 (1974).

Address of Hoke, Hawkins, and Shaw: Department of Physics, 174 West 18th Ave., The Ohio State University, Columbus, Ohio, 43210.

ME6. (2:40)

LINE PARAMETERS FOR THE 5-µm BANDS OF CARBON DIOXIDE

C. P. RINSLAND, D. C. BENNER, D. J. RICHARDSON, AND M. A. H. SMITH

Positions and intensities of carbon dioxide lines in the 1830-2010 cm^{-1} region have been measured from long-path, low-pressure ($P < 10$ Torr) 0.01-cm^{-1} resolution spectra recorded at room temperature with the Fourier transform spectrometer in the McMath solar telescope complex at Kitt Peak National Observatory. Over 96 percent of the 1038 lines observed have been assigned to bands of $^{12}C^{16}O_2$, $^{13}C^{16}O_2$, $^{12}C^{16}O^{18}O$, $^{12}C^{16}O^{17}O$, and $^{13}C^{16}O^{18}O$ or identified as residual lines of H_2O. The weakest carbon dioxide lines have intensities of $\approx 0.5 \times 10^{-26}$ cm/molecule at room temperature. A preliminary analysis of the data has been published in the form of an atlas of observed spectra with tabulated observed and calculated line positions and assignments.[1]

In this talk, the absolute intensity measurements are discussed. Values have been derived for selected unblended lines with a nonlinear least squares curve fitting procedure. Intensities determined from spectra recorded with different pressure-path length combinations agree to $\approx$ 1 percent for the stronger lines. The intensity data have been analyzed to determine vibrational band intensities and F-factor coefficients for the stronger bands.

[1] D. C. Benner, C. P. Rinsland, D. J. Richardson, T.-H. Soo, and M. A. H. Smith, NASA Technical Memorandum 84612, 1983.

Address of Rinsland and Benner: Department of Physics, College of William and Mary, Williamsburg, VA, 23185. Richardson: Systems and Applied Sciences Corporation, Hampton, VA 23665. Smith: NASA Langley Research Center, Mail Stop 401A, Hampton, VA 23665

ME7. (2:52)

MOLECULAR CONSTANTS OF $^{12}C^{16}O_2$ BANDS IN 1900 cm^{-1} ∿ 2150 cm^{-1}

HAJIME SAKAI

The CO_2 exhibits several bands of medium strength in 1900 cm^{-1} ∿ 2150 cm^{-1}. In decreasing order of the band strength (at room temperature), they are [11101-00001] band centered at 2076.9 cm^{-1}, [11102-00001] at 1932.5 cm^{-1}, [12201-01101] at 2093.3 cm^{-1}, [20001-01101] at 2129.8 cm^{-1}, and so forth. The molecular constants determined for these perpendicular bands provide a useful check for consistency in the global molecular constants of CO_2. The absorption data observed at gas temperature of 300°K were used to obtain a wide J coverage in the transition. The molecular parameters which are determined consistent with other observed transitions are shown in Table I.

Table I

	G	B	D	H
00001	0.000	.39021894	1.33373×10^{-7}	$.1600 \times 10^{-13}$
01101C	667.380	.39063975	1.35766	.7348
01101D	667.380	.39125482	1.36069	.0233
11102C	1932.471	.39074417	1.49141	.6070
11102D	1932.471	.39168843	1.55135	-.3247
11101C	2076.856	.39040975	1.25920	1.0431
11101D	2076.856	.39133492	1.21724	1.8109
12201C	2760.725	.39154703	1.41812	-5.6429
12201D	2760.725	.39154703	1.28067	.8724
20001	2797.136	.39060518	.97501	4.6544

This work was supported in part by AFOSR under AFGL Contract No. F19628-81-K-0007.

Address: Astronomy Research Facility, University of Massachusetts, Amherst, Massachusetts 01003, U.S.A.

MF8. (3:15)

$^{12}C^{16}O^{18}O$: HIGH RESOLUTION EMISSION SPECTRA BY FOURIER TRANSFORM SPECTROSCOPY (FROM 2000 TO 2400 CM^{-1})

D. BAILLY, *G. GUELACHVILI* and *C. ROSSETTI*

In order to study the vibrational levels of the CO_2 molecule and those of its main isotopic species, the emission spectra of CO_2-N_2, CO_2-N_2-He gas mixtures excited by d.c. discharge have been recorded with a Fourier Transform Spectrometer (Resolution : 5.4 $10^{-3}cm^{-1}$) between 1700 and 2400 cm^{-1}.

The vibrational luminescence of 6 isotopic species $^{12}C^{16}O_2$, $^{12}C^{18}O_2$, $^{13}C^{16}O_2$, $^{13}C^{18}O_2$, $^{12}C^{16}O^{18}O$ and $^{13}C^{16}O^{18}O$, have been observed : for each one, thousands of lines from band sequences $v_1 v_2^{\ell} v_3 \to v_1 v_2^{\ell}(v_3-1)$ have been assigned.

Results from symmetric molecules have been reported in previous papers. We shall present results obtained from the analysis of 15 vibrational transitions concerning the assymmetric species $^{12}C^{16}O^{18}O$.

We shall give the spectroscopic constants associated with the 33 vibrational levels or sublevels observed ; these constants allow us to reproduce the experimental wavenumbers with a standard deviation $< 8\ 10^{-5}cm^{-1}$, the best being $4\ 10^{-5}cm^{-1}$.

Address : Laboratoire d'Infrarouge, Université de Paris-Sud, Bâtiment 350, 91405 Orsay Cédex, France.

ME9. (3:32)

ANALYSIS OF Δv_3= 1 BANDS OF 800K $^{13}C^{16}O_2$ AND $^{13}C^{16}O^{18}O$

MARK P. ESPLIN AND LAURENCE S. ROTHMAN

High temperature absorption spectra of an isotopically enriched sample of CO_2 has been measured in the 4.3μm region using the Air Force Geophysics Laboratory (AFGL) high resolution interferometer. A maximum optical path difference of 75 cm was used, resulting in an unapodized spectral resolution of about 0.007 cm^{-1}. Due to the difficulty in making positive identification of spectral lines in the dense experimental spectra, only those bands with a lower state vibrational term value less than 1400 cm^{-1} for $^{13}C^{16}O_2$ and the fundamental of $^{13}C^{16}O^{18}O$ had previously been identified[1]. Additional bands of these two isotopes have now been identified in the experimental spectra. Vibration-rotation constants which predict the position of spectral lines of these bands with an estimated accuracy of 0.0004 cm^{-1} will be presented.

[1]M.P. Esplin, R.J. Huppi and G.A. Vanasse, Appl. Opt. 21, 1681 (1982).

This work was supported by the Air Force Office of Scientific Research.

Address of Esplin: Stewart Radiance Laboratory, Utah State University, 139 The Great Rd., Bedford, Massachusetts 01730.
Address of Rothman: Optical Physics Division, U.S. Air Force Geophysics Laboratory, Hanscom Air Force Base, Massachusetts 01731.

ME10. (3:44)

TUNABLE DIODE LASER MEASUREMENTS OF INTENSITIES AND SELF-BROADENED WIDTHS OF THE 00°1 - 10°0 BAND OF N_2O

C. A. DEJOSEPH, JR. AND D. R. POND

Intensities and self-broadened widths of 48 N_2O lines of the V_3 - V_1 band centered at 939 cm^{-1} have been measured using a tunable diode laser. Intensities and widths for each line were determined by least-squares fitting Voigt profiles to measured room temperature absorbances at four pressures over the range 20 -200 torr in a 2.4 meter absorption cell. Broadening coefficients up to $|m|$ = 33 were obtained. Intensities were corrected to 300°K and using relative intensity calculations an average band intensity of $(4.77 \pm 0.04) \times 10^{-2}$ cm^{-2} atm^{-1} was obtained. This is about 20% less than the band intensity used in the AFGL data compilation.

Address of DeJoseph and Pond: AFWAL/POOC-3, Wright-Patterson AFB OH 45433

ME11. (3:56)

INTENSITIES AND COLLISIONAL LINEWIDTHS OF N_2O FROM FOURIER TRANSFORM SPECTRA

N. LACOME, A. LEVY and G. GUELACHVILI

A method giving simultaneously the linestrengths and linewidths from Fourier transform spectra has been set up[1]. It was applied to determine the intensities of four transitions of N_2O : the 20^00 - 00^00 and 12^00 - 00^00 near 4 μm
the 10^00 - 00^00 and 02^00 - 00^00 near 8 μm.
The self, N_2 and O_2 broadening coefficients have also been measured at 300°K and 220°K. Good agreement is shown with theoretical values calculated using an improved formalism without resort to any cut-off procedure[2].

[1] N. LACOME, A. LEVY, C. BOULET and J.P. HOUDEAU, Applied Optics 21, 2473-2480 (1982).

[2] N. LACOME, A. LEVY and C. BOULET, J. Mol. Spectrosc. 97, 139-153 (1983).

Address : Laboratoire d'Infrarouge, Bât. 350, Université de Paris-Sud, 91405 Orsay Cédex, France.

ME12. (4:13)

TEMPERATURE DEPENDENCE OF THE O_2-BROADENED LINE WIDTHS OF N_2O

R. L. HAWKINS, J. H. SHAW

Oxygen-broadened line widths of the $\nu_1 + 2\nu_2$ band of N_2O have been obtained for temperatures as low as 235 K. Fourier transform spectra, at a resolution of 0.07 cm^{-1} apodized, were taken of long path length (131 m) samples of N_2O broadened by oxygen. The spectra were analyzed by the nonlinear least-squares, whole-band analysis technique. Lorentz widths for $|m|$=1 to 40 were obtained at several temperatures.

Address: Department of Physics, The Ohio State University, Columbus, Ohio, 43210.

ME13. (4:25)

THEORETICAL DETERMINATION OF N_2-BROADENED HALFWIDTHS OF OZONE

R.R. GAMACHE, R.W. DAVIES, and L.S. ROTHMAN

For $^{16}O_3$, accurate N_2-broadened halfwidths are difficult to obtain for a large number of transitions. Recent measurements[1] have allowed assigning average air-broadened halfwidths of ozone for A-type bands, α = 0.083 cm^{-1}/atm, and for B-type bands, α = 0.077 cm^{-1}/atm at 296K. These measurements, however, were not extensive enough to give J-dependence of the halfwidths. Theoretical N_2-broadened halfwidths have been determined for a number of ν_3 (A-type) and ν_1 (B-type) transitions of ozone. The halfwidths have been evaluated using the Anderson-Tsao-Curnutte theory of collisional-broadening and by the more rigorous Quantum Fourier Transform theory due to Davies.[2] In the calculations, contributions to the halfwidth from dipole-quadrupole interaction and quadrupole-quadrupole interaction are considered. Both methods are compared with experiment. From the study, air-broadened halfwidths will be calculated for an extensive list of transitions for ozone, and these will appear on a future AFGL Main Gas Compilation.

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1. J.M. Hoell, C.N. Harward, C.H. Bair, and B.S. Williams, Opt. Eng. 21, 548(1982); J.S. Margolis, Appl. Opt. 21, 3109(1982).
2. R.W. Davies, Phys. Rev. A12, 927(1975).

This work was supported by the Air Force Office of Scientific Research, through AFGL task 2310G1.

Address of Gamache: The Center for Atmospheric Research, University of Lowell Research Foundation, 450 Aiken Street, Lowell, MA 01854.

Address of Davies: GTE/Sylvania, 40 Sylvan Road, Waltham, MA 02154.

Address of Rothman: Optics Division, Air Force Geophysics Laboratory, Hanscom AFB, MA 01731

ME14. (4:37)

DIODE LASER LABORATORY SPECTROSCOPY SUPPORTING THE 12μm HETERODYNE DETECTION OF C_2H_6 ON JUPITER [1]

D. E. JENNINGS

Observational infrared spectroscopy of planetary atmospheres presently employs instrumentation capable of spectral resolution equaling that of any technique available in the laboratory. The CO_2 laser heterodyne spectrometer has been used to observe planetary spectra at resolutions of 10^{-4} cm^{-1}. The recently reported detection of stratospheric ethane on Jupiter near 12μm using infrared laser heterodyning[1] required a coordinate laboratory effort to provide line parameters from diode laser spectra. A diode laser spectrometer was used to determine individual frequencies and strengths for lines in the ν_9 band of ethane which might be observed using the heterodyne technique. Lines of ethane in the 12μm region not belonging to ν_9 were also identified. This study is part of a more general analysis[2] of ν_9 using diode laser and FTS spectra.[2]

The present configuration of the diode laser spectrometer includes several innovations not described previously. Techniques for measuring line frequencies and strengths will be presented. Confocal etalons of 50 and 2.5 cm length have been evaluated for use in calibration and spectral analyses of diode laser output; the longer etalon provides a fringe pattern with 150 MHz free-spectral-range and fringe widths limited by the laser output width. A method for rapid sweep-integration of second derivative spectra also has been developed.

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[1] T. Kostiuk, M. J. Mumma, F. Espenak, D. Deming, D. E. Jennings, and W. Maguire, Ap.J. 265, 564 (1983).

[2] J. Susskind, D. Reuter, D. E. Jennings, S. J. Daunt, W. E. Blass, and G. W. Halsey J. Chem. Phys. 77, 2728 (1982); S. Daunt, A. Atakan, W. Blass, G. Halsey, D. Jennings, D. Reuter, J. Susskind, and J. Brault, submitted (1983).

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ME15. (4.54)

HIGH RESOLUTION FOURIER TRANSFORM SPECTRA OF THE ν_1 BAND OF HYDRAZOIC ACID (HN_3)

A. S-C. CHEUNG AND A. J. MERER

The ν_1 (N-H stretching) fundamental of HN_3 between 3140 cm^{-1} and 3600 cm^{-1} has been recorded at a resolution of 0.004 cm^{-1} using a Fourier transform spectrometer. This is a type AB hybrid band of a slightly asymmetric top, where the K-type doubling is resolved up to K = 4. Two sets of K' = 1 sub-bands are observed, indicating an upper state perturbation.

In the present work, combination differences between different K'' levels can be measured directly for K'' up to 7; they can be combined with previous microwave measurements[1] to give improved molecular constants for the ground state.

The analysis of the weak, badly perturbed $\nu_2 + \nu_4$ combination band at 3250 cm^{-1} will also be discussed.

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[1] J. Bendtsen and M. Winnewisser, Chem. Phys. Letters 33, 141 (1975).

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MF1. (1:30)

LINE ASSIGNMENTS IN THE H-F STRETCHING FUNDAMENTALS OF THE HF DIMER

W. J. LAFFERTY AND A. S. PINE

Line assignments in the two H-F stretching fundamentals have been extended considerably over those reported at this meeting last year. Only b-type transitions have been observed for the higher frequency ν_1 band centered at $\sim$3929 cm^{-1} while only a-type transitions have been assigned for the ν_2 band at 3868 cm^{-1}. The KΔK = -2, -1, 0, + 1, and +2 subbands of the ν_1 band have been assigned. The upper states of the KΔK = 1 subband of this vibration are perturbed. At this moment only the K=0 and K=1 subbands of the parallel band have been assigned.

The molecule is very non-rigid, and it is necessary to fit each subband independently using a Polo formalism. As in other very near prolate top molecules, the asymmetric rotor splitting of the K=2 states has been found to be anomalously large. The inversion splitting in the upper state of both bands is about one third that of the ground state.

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MF2. (1:47)

MILLIMETER WAVE INVESTIGATION OF THE HF DIMER

R. D. SUENRAM, F. J. LOVAS, AND W. J. LAFFERTY

The rotation-inversion spectrum of the ground state of the HF dimer has been studied in a one meter stainless steel cell under equilibrium conditions at dry ice temperature in the frequency region of 60 to 125 GHz. Both K=0 and K=1 subband transitions have been observed, thus extending the previous observations[1,2] to higher J. In addition, with the aid of infrared combination differences, 13 P, Q, and R lines of the K=2 subband have been identified.

A fit of the higher J K=0 and K=1 subband lines observed in this work as well as those previously measured,[1,2] yields improved values for the centrifugal distortion constants. The observed microwave K=2 lines were combined with infrared combination differences to obtain the spectroscopic constants of the K=2 state. The inversion spitting and B rotational constants for this state are:

ν_{2} inv.	60073.39(11)	MHz
B^-	6551.106(12)	MHz
B^+	6553.721(12)	MHz
$E_2^+-E_0^+$	116.13329(8)	cm^{-1}

where the + or - sign indicates respectively the lower or upper tunnelling component and $E_2^+-E_0^+$ is the energy difference between the hypothetical J=0 level of the K=2 state and the ground state. Not unexpectly the centrifugal disortion constants for the K=2 levels are found to be anamolously large. Because of the nonridigity of the molecule it is necessary to treat each subband independently.

[1] T. R. Dyke, B. J. Howard and W. Klemperer, J. Chem. Phys. 56, 2664 (1972).

[2] B. J. Howard, T. R. Dyke, and W. Klemperer, private communications.

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MF3. (2:04)

MILLIMETER WAVELENGTH STUDY OF THE HF-H_2CO SYSTEM

F. J. LOVAS AND R. D. SUENRAM

Recently Baiocchi and Klemperer[1] have reported the microwave spectrum of H_2CO-HF from a molecular beam electric resonance study. We have examined this system with a conventional waveguide Stark-modulated absoption cell in order to see if this species could be produced under thermal equilibrium conditions and to obtain further information about higher energy states which are not accessible in a cooled beam experiment. Both the cell and experimental conditions were similar to that described for the HF-dimer[2]. With the aid of the molecular beam data[1] we have identified numerous a-type R-branch transitions up to J=13 and K=8. A combined analysis of the molecular beam spectrum and the present data requires inclusion of several P^6 terms in the Watson Hamiltonian in order to fit the higher K transitions.

A much stronger spectrum was observed in the region searched (~ 70 - 125 GHz). This has been analyzed and assigned to a reaction product of H_2CO with HF, namely gauche-CH_2FOH. Both a- and b- type transitions are observed and occur as closely spaced doublets quite similar to gauche-CH_3CH_2OH[3]. Futher details of the measurements between 70 GHz and 125 GHz and analyses for each species will be presented.

[1] F. A. Baiocchi and W. Klemperer, preprint 1983.

[2] R. D. Suenram, F. J. Lovas, and W. J. Lafferty, previous talk this session.

[3] R. Kakar and C. R. Quade, J. Chem. Phys., 72, 4300 (1980).

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MF4. (2:21)

MILLIMETER AND SUBMILLIMETER SPECTROSCOPY OF MOLECULAR IONS IN A NEW MAGNETICALLY ENHANCED SOURCE*

GRANT M. PLUMMER, GEOFFREY A. BLAKE, WAYNE C. BOWMAN, ERIC HERBST, AND FRANK C. DE LUCIA

A new method for the microwave absorption spectroscopy of molecular ions has been developed. In this system an axial magnetic field of ~200 Gauss is used to lengthen the negative glow region of a discharge to fill the length of an absorption cell. We find that ion densities are enhanced by approximately two orders of magnitude. This system has been used to observe in natural abundance $H^{12}C^{18}O^+$ (in real time on an oscilloscope) and $H^{12}C^{17}O^+$. In addition, the molecular ions $^{14}N^{16}O^+$ and $^{40}ArD^+$ have been observed. The spectra of these two species are one to two orders of magnitude weaker than that of the "standard" molecular ions $H^{12}C^{16}O^+$, $H^{14}N_2^+$, etc. $^{36}ArD^+$ and $^{38}ArD^+$ have also been observed in natural abundance. Spectroscopic constants and details of the experimental method will be given.

*Work supported by NASA Grant NAGW-189.

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MF5. (2:38)

MICROWAVE SPECTROSCOPY OF WATER BETWEEN 500 GHz and 1000 GHz*

JAMES K. MESSER, PAUL HELMINGER, AND FRANK C. DE LUCIA

A number of previously unreported rotational transitions in the ground and first excited vibrational state of H_2O, HDO, and D_2O between 500 GHz and 1000 GHz have been observed. The fundamental source of radiation was a reflex klystron operating at about 50 GHz, which was used to drive a crossed-waveguide harmonic generator. The new transitions were combined with previously reported results, and fitted to a centrifugal distortion Hamiltonian in order to obtain spectral parameters.

*Work supported by ARO Grant DAAG-29-80-C-0026 and NASA Grant NSG-7574.

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MF6. (3:10)

EXCITATION MECHANISMS IN THE HCN FIR LASER*

DAVID D. SKATRUD, GEOFFREY A. BLAKE, K.V.L.N. SASTRY, AND FRANK C. DE LUCIA

A number of excitation mechanisms have been proposed to explain the behavior and efficiency of the HCN FIR laser. We have used millimeterwave spectroscopic techniques to probe this excitation. The effects due to the addition of CO on the distribution of vibrational excitation and laser efficiency have been studied. We have also observed the concentration of proposed chemical precursors, including the free radical CN. A spectroscopic study of $^2\Sigma$ CN is also reported. 65 new lines in the first 4 vibrational states have been measured. A simultaneous non-linear least squares fit of these data, along with those previously reported by Dixon and Woods[1], has been carried out.

*Work supported by ARO Grant DAAG-29-80-C-0026 and NASA Grant NAGW-189.
[1]T.A. Dixon and R.C. Woods, J. Chem. Phys. 67, 3956-3964 (1977).

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MF7. (3:27)

ENERGY TRANSFER MECHANISMS AND TWO PHOTON EFFECTS IN $^{13}CH_3F$*

WILLIAM H. MATTESON, DAVID D. SKATRUD, AND FRANK C. DE LUCIA

Energy transfer mechanisms and collisional processes have been studied in the $^{13}CH_3F$ optically pumped Far Infrared laser by means of millimeterwave spectroscopy. A model based upon a master equation approach is used to fit these experimental results in terms of energy transfer probabilities. This model then is used to predict the performance of an optically pumped laser as a function of pressure, pump rate, and cavity parameters. We have also investigated two photon processes in $^{13}CH_3F$. In these experiments an RF field is applied in addition to the CO_2 pump and the millimeter diagnostic probe.

*Worked supported by the Army Research Office, Grant DAAG-29-80-C-0026.

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MF8. (3:44)

TONE-BURST MODULATION COLOR CENTER LASER SPECTROSCOPY

CHRISTOPHER S. GUDEMAN, MARIANNE H. BEGEMANN, JÜRGEN PFAFF, AND RICHARD J. SAYKALLY

The technique of tone-burst modulation has been developed by Pickett[1] as a general scheme for high sensitivity microwave absorption spectroscopy. This method has been used very successfully by Woods and co-workers[2] for the detection and study of transient species in DC glow discharges. We report in this paper the extension of the tone-burst technique to tunable infrared laser absorption spectroscopy (2.2-3.3 μm) using a color center laser and an extracavity $LiTaO_3$ phase modulator. The tone-burst consists of a ~50 watt RF "tone" (100-400 MHz) which is amplitude modulated at 100 kHz with a depth of 100%, and is applied to the phase modulator. The infrared laser radiation which traverses the modulator crystal is then composed of the original infrared carrier plus sidebands which are switched on and off at 100 kHz and are separated from the carrier by the tone frequency. Simple lock-in signal processing at the 100 kHz burst rate then provides high sensitivity.

By observing several R, P, and Q branch NO $v = 0 \rightarrow 2$ overtone transitions, a minimum detectable absorption of .05% has been determined. This is limited by power fluctuations resulting from standing waves in the infrared path; thus the laser and detector noise limits have not yet been reached, and further improvements in sensitivity are anticipated. We have also observed several OH $v = 0 \rightarrow 1$ transitions in a DC glow discharge through H_2O. The $R(3/2)_{2+}$ transitions at 3663.7 cm^{-1} were observed with S/N > 100 under the following conditions: 500 mTorr H_2O, 30 mA/cm discharge current density, 100 msec time constant, 40 sec scan, and 400 MHz tone frequency. The linewidth is broader than thermal Doppler width due to unresolved hyperfine structure.

The adaptation of tone-burst modulation to tunable infrared absorption spectroscopy is a simple but powerful technique, since it results in high sensitivity with conventional instrumentation (e.g., lock-in amplifiers).

[1]H. M. Pickett, Applied Optics, 19, 2745 (1980).

[2]C. S. Gudeman and R. C. Woods, Phys. Rev. Lett. 48, 1344 (1982).

* Supported by NSF Grant # CHE 8207307.

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MF9. (3:54)

VELOCITY MODULATED LASER ABSORPTION SPECTROSCOPY OF MOLECULAR IONS

CHRISTOPHER S. GUDEMAN, MARIANNE H. BEGEMANN, AND RICHARD J. SAYKALLY

Doppler shifts in the transition frequencies of molecular ions produced in DC glow discharges were first reported by Woods and co-workers[1] for pure rotational spectra in the 3 mm region. These Doppler shifts were ~10 times smaller than the pressure broadened linewidths and were therefore too small to produce well-resolved red- and blue-shifted components, which could provide velocity modulation of absorption signals for lock-in detection. Because pressure broadening is usually negligible at infrared wavelengths, and high ion velocities ($v_{drift} \approx v_{random}$) can be realized in light gases such as H_2 and He, velocity-modulated ion absorption spectroscopy in audio frequency discharges with lock-in detection at the discharge frequency becomes a straightforward and powerful technique for ion absorption spectroscopy when used in conjunction with a narrow bandwidth tunable laser source. Absorptions due to neutral atoms and molecules, which are much more abundant in these discharges than charged species, are suppressed by about a factor of 100. Furthermore, a first derivative line shape is characteristic of ion signals, while a single Gaussian shape is observed for neutrals, providing unambiguous differentiation between charged and neutral spectra.

In this paper we describe a velocity modulation absorption spectrometer which consists of a commercial color center laser (Burleigh FCL-20), an 1 cm x 1 m liquid nitrogen cooled AC discharge cell, an InSb photovoltaic detector, and a lock-in amplifier. Operating characteristics, including sensitivity, lineshapes, and spectral and dynamical information obtained, will be discussed. The extension of this method to absorption spectroscopy with visible dye lasers will be described.

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[1] R. C. Woods, T. A. Dixon, R. J. Saykally, and P. G. Szanto, Phys. Rev. Lett. 35, 1269 (1975); C. S. Gudeman, N. D. Piltch, and R. C. Woods, 37th Symposium on Molecular Spectroscopy, Columbus, OH, June 1982, paper TB7.

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MF10. (4:09)

MEASUREMENT OF THE ν_1 BAND OF HCO^+

CHRISTOPHER S. GUDEMAN, MARIANNE H. BEGEMANN, JÜRGEN PFAFF, AND RICHARD J. SAYKALLY

Using the technique of velocity modulated laser absorption spectroscopy and a color center laser, the ν_1 fundamental band of HCO^+ has been measured. This method involves modulating the drift velocity of the ion in an AC discharge (~2.5 kHz) and detecting the Doppler shifted absorptions with lock-in techniques. HCO^+ was detected with a H_2/CO ratio of 10/1 and a total pressure of ~1 torr. A least squares fit of the 25 lines that were observed yielded values for ν_0(3088.727 cm^{-1}), and for B", D", B' and D' that are in excellent agreement with results from microwave spectroscopy.

* Supported by NSF Grant # CHE8207307

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MF11. (4:26)

MEASUREMENT OF THE ν_1 BAND OF HNN^+

MARIANNE H. BEGEMANN, CHRISTOPHER S. GUDEMAN, JÜRGEN PFAFF, AND RICHARD J. SAYKALLY

The ν_1 fundamental band of HNN^+ (ν_0 = 3233.954 cm^{-1}) has been detected using a color center laser and the same modulation method that was used to measure the ν_1 band of HCO^+: velocity modulation in an AC discharge. HNN^+ was observed in the flowing AC discharge with a H_2/N_2 ratio of 10/1 and a total pressure of ~1 torr. A total of 43 lines were measured and a least squares fit was used to determine the molecular constants ν_0, B", D", B' and D'. The HNN^+ spectrum could also be observed in a NH_3/H_2 discharge where the suppression of neutral lines using this modulation technique is clearly demonstrated.

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MF12. (4:43)

ULTRAVIOLET LASER INDUCED FLUORESCENCE SPECTROSCOPY OF MOLECULAR IONS IN A RADIOFREQUENCY ION TRAP

CECILIA MARTNER, JÜRGEN PFAFF, NEIL ROSENBAUM, AND RICHARD J. SAYKALLY

The application of laser induced fluorescence spectroscopy to measure electronic spectra of molecular ions confined in a radiofrequency ion trap was pioneered by Mahan and co-workers,[1] who used visible lasers to study LIF spectra of CH^+, CO^+, N_2^+, $BrCN^+$, H_2S^+, hexafluorobenzene, and 1,3,5-trifluorobenzene cations. We have extended this technique into the ultraviolet (218-350 nm) through the use of a Nd-YAG-pumped dye laser system with nonlinear crystals permitting frequency doubling and mixing with the YAG-fundamental.

The 0,0 band of the $A^2\Sigma^+ - X^2\Sigma^+$ system of CO^+ was observed at wavelengths near 219 nm. These measurements were obscured by the presence of a continuous background fluorescence, that varied approximately as the cube of the ultraviolet intensity. This as yet unidentified non-linear background was minimized by operating at the lowest laser powers that produced detectable A-X fluorescence. The 1,3 band of the similar $B^2\Sigma^+ - X^2\Sigma^+$ transition of N_2^+ was recorded near 330 nm.

The 0,0 and 1,0 bands of the $A^2\Sigma^+ - X^2\Pi_{3/2}$ systems of HCl^+ and HBr^+ were recorded near 350 nm and 330 nm, respectively. Rotational state-resolved radiative lifetimes were measured for low-J states of each ion. No J-variation in the lifetimes is apparent. For HCl^+, τ = 3.2 ± .4 and for HBr^+ τ = 3.9 ± .2, in reasonable agreement with measurements of unresolved vibronic bands.

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[1] F. J. Grieman, B. H. Mahan, A. O'Keefe, and J. S. Winn, Faraday Disc. 71, 191 (1981).

* Supported by NSF Grant # CHE 8207307.

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MF13. (5:00)

Doppler Shift and Ion Mobility Measurements of ArH^+ in a He DC Glow Discharge by Diode Laser Spectroscopy

Nathan N. Haese, Fu-Shih Pan, and Takeshi Oka

We have measured the drift velocity and the mobility of ArH^+ ions in a helium DC glow discharge by observing the drift velocity induced Doppler effect frequency shifts of the ions infrared absorption lines at 4 μm.[1] The shifts are comparable to the line width, ~100 MHz, and correspond to a drift velocity of ~4×10^4 cm s^{-1}. From pressure, temperature, and axial electric field measurements we obtain a reduced mobility of ArH^+ in He of 19 ± 4 (2σ) $cm^2/(V\text{-}s)$ which is in excellent agreement with the earlier mass spectroscopic drift tube result of 19.2 ± 1.6 $cm^2/(V\text{-}s)$.[2] Preliminary tests of the ArH^+ v and J dependence of the Doppler shift have been made.

1. J.W. Brault and S.P. Davis, Phys. Scrip. 25 268 (1982).

2. W. Lindinger and D.L. Albritton, J. Chem. Phys. 62 3517 (1975).

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MG1. (1:30)

TWO LASER FRAGMENTATION STUDY OF BUTADIENE

A. M. Woodward, S. D. Colson, W. A. Chupka, and M. S. Seaver

Fragmentation of the 1,3-trans-Butadiene ion formed by two-photon resonant multiphoton ionization has been investigated utilizing two separate tunable lasers. The butadiene ion is formed by resonantly pumping the 0-0 transition of the 3s Rydberg state at 399.1 nm. This forms the parent ion predominantly in the vibrationless ground state which can be verified by the photoelectron spectrum.

Fragmentation of the parent ion has been studied using a single laser as a function of laser power and the kinetic energy release of the fragments has been measured by varying the initial acceleration voltage.

A second laser at 495.00 nm is used to photodissociate the parent ion. The resulting fragmentation can be explained on the basis of the breakdown curves[1] and the photoelectron spectrum.[2] A metastable peak is observed in the two laser mass spectrum at low dissociation laser power which decreases in intensity as the power is increased. By scanning the second laser the absorption spectrum of the ion can be taken.

[1]J. Dannacher, J. Flamme, J. Stadelmann and J. Vogt, Chem. Phys. 51(1980)189. [2]K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki and S. Iwata, Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules (Halsted Press, New York, 1981) p.62.

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MG2. (1:47)

PREPARATION AND PHOTODISSOCIATION OF CH_3I^+ BY MULTIPHOTON PROCESSES

A. M. Woodward, S. D. Colson, W. A. Chupka, and M. S. Seaver

Two-photon resonant multiphoton ionization has been used to prepare rotationally cooled and selected CH_3I^+ ions with controlled vibrational and electronic distributions. These ions are photodissociated by a second laser. The highly simplified photodissociation spectrum displays a clear dissociation threshold as well as bands hidden in earlier spectra. The data suggest corrections to previously determined vibrational constants.

The electronic transition studied corresponds to excitation of a nonbonding 5pπ electron to a 6s molecular Rydberg orbital on an ion core of the ground configuration. The bare ion core in this configuration has $^2\pi_{1/2}$ and $^2\pi_{3/2}$ states which are separated by about 5000 cm^{-1} by strong spin orbit coupling. Time-of-flight photoelectron spectroscopy has been used to study the branching ratio of the channels to $\pi_{1/2}$ and $\pi_{3/2}$ ionization.

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MG3. (2:04)

RESONANT MULTIPHOTON IONIZATION AND ELECTRON IMPACT SPECTROSCOPIC INVESTIGATIONS OF DIENES

A. SABLJIĆ, R. MCDIARMID, AND J. P. DOERING

A combination of the data obtained by resonant multiphoton ionization and electron impact spectroscopies has been exploited to enable Rydberg and valence transitions to be experimentally distinguished and to permit optically forbidden transitions to be located. The technique was verified on 2,3-dimethylbutadiene, whose transitions could be characterized by electron impact results alone, and then applied to seven internally and externally methyl substituted dienes in both the s-cis and s-trans configurations. It was possible to locate the NV_2 (A_g) transition in 6 of the studied molecules. The effect of symmetry and methyl substitution on the valence and Rydberg transitions of these dienes will be discussed.

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MG4. (2:21)

ELECTRONIC SPECTRA OF CONCENTRATED SOLUTIONS

LEIGH B. CLARK

Light reflected at the boundary between a transparent window and an absorbing liquid solution is related to the complex index of refraction of the solution which is derived from the absorption spectrum of the solution. Since the solution absorption spectrum is (for the most part) a superposition of the absorption spectra of both the solute and the solvent, information about the individual component absorption spectra is contained in the reflection spectrum obtained from such a boundary. In particular for very concentrated solutions, concentrated solutions in the region of solvent absorption and for other optically dense systems such reflection spectra would seem to be a useful probe.

Preliminary data for light reflected from interfaces between either quartz or LiF and concentrated solutions of several hydrocarbons dissolved in various solvents will be presented for the visible, UV and vacuum UV regions and for transparent and absorbing solvents.

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MG5. (2:28)

POLARIZED ELECTRONIC SPECTRA OF PYRIMIDINES

JOEL NOVROS, FRANK ZALOUDEK, AND LEIGH B. CLARK

Polarized reflection spectra from single crystals of cytosine monohydrate, 1-methylthymine, thymine anhydrate and 1-methyluracil have been measured in the range 350-135 nm. Absorption spectra obtained by Kramers-Kronig analysis give evidence for the transition moment directions of the first four or five strong electronic transitions of these systems.

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MG6. (2:40)

TIME-RESOLVED FLUORESCENCE DEPOLARIZATION IN THE DECAY OF INTERMEDIATE CASE MOLECULES. ZERO-FIELD LEVEL CROSSING OF THE MOLECULAR EIGENSTATES OF $^1B_{3u}$ PYRAZINE *

Y. MATSUMOTO, L. H. SPANGLER, AND D. W. PRATT

Pyrazine (1,4-diazabenzene) has been expanded in a seeded supersonic jet of helium and its laser induced fluorescence spectrum recorded following pulsed (and doubled) dye laser excitation to the first excited 'singlet' state. Under these conditions, the decay of the fluorescence is biexponential in character, as expected for an 'intermediate-case' molecule. Studies of this decay with simultaneous analysis of the polarization of the emitted light, under 'single' rotational level excitation conditions, show that the emission is depolarized nonexponentially in time. This behavior is attributed to dephasing processes by which the initial, non-stationary state evolves into a group of phase incoherent molecular eigenstates, and thus its observation constitutes proof of the coherent nature of the excitation process.

* Work supported by the National Science Foundation.

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MG7. (3:10)

ON THE ORIGIN OF THE ROTATIONAL STATE DEPENDENCE OF THE DECAY OF $^1B_{3u}$ PYRAZINE. ANGULAR MOMENTUM SELECTION RULES IN INTERSYSTEM CROSSING [1]

Y. MATSUMOTO, L. H. SPANGLER, AND D. W. PRATT

$^1B_{3u}$ Pyrazine, as noted above, exhibits a fluorescence decay which is biexponential in character. Studies of this decay under collision-free conditions reveal a strong rotational state dependence of the A^+/A^- ratio, as first reported two years ago at this conference.[2] We now describe further experiments which show that, under nanosecond excitation conditions, A^+/A^- scales as $2J' + 1$ but τ^+ and τ^- are J' independent. By considering the spin-orbit properties of triplet pyrazine in the condensed phase, and transforming the problem into the gas phase, we then demonstrate that this behavior is to be expected whenever J (the total angular momentum quantum number), but not P (the projection of J on the top axis), is conserved in the intersystem crossing process. Some possible origins of the breakdown in the $\Delta P = 0$ selection rule will be discussed.

[1] Work supported by the National Science Foundation.

[2] G. ter Horst, J. Kommandeur, and D. W. Pratt, 36th Symposium on Molecular Spectroscopy, June, 1981, Paper FB10.

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MG8. (3:27)

MAGNETIC FIELD EFFECTS ON THE DECAY OF $^{1}B_{3u}$ PYRAZINE IN A SUPERSONIC JET *

L. H. SPANGLER, Y. MATSUMOTO, AND D. W. PRATT

In this work, we will show that the decay of 'single' rotational levels of the first excited 'singlet' state of pyrazine can also be influenced by small magnetic fields, thereby demonstrating that the coupled state is triplet in character. Under nanosecond excitation conditions, we find that neither τ^+ nor τ^- are field dependent, but that A^+/A^- increases in a sigmoidal fashion with the field, reaching a plateau at $H \sim 100$ G for all J' from 1-7. However, the decay of the $J' = 0$ level shows no magnetic field dependence. This result, together with the results of similar studies of isotopically labeled pyrazines, suggests that the levels which are mixed by the field are the fine-structure components of the triplet state, which results in a breakdown of the $\Delta J = 0$ selection rule for intersystem crossing. The possible reasons for this behavior at such low fields will be discussed.

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MG9. (3:44)

LASER INDUCED FLUORESCENCE EXCITATION SPECTRA OF 1-FLUORO, 1-CHLORO, AND 1-BROMONAPHTHALENE IN A SUPERSONIC JET [1]

M. V. RAMAKRISHNA AND D. W. PRATT

The 1-halonaphthalenes have played a central role in the development of our understanding of the role of spin-orbit coupling in photophysical processes [e.g., intersystem crossing (ISC)] in the condensed phase. In this work, we examine the interesting possibility that more detailed information about the dynamics of such processes can be obtained from experiments on the isolated molecule. Toward this end, we have obtained vibronically resolved laser induced fluorescence excitation spectra of 1-fluoronaphthalene (1FN), 1-chloronaphthalene (1CN), and 1-bromonaphthalene (1BN) in seeded supersonic jets of helium, and compared the results with those of similar experiments on the parent molecule.[2,3] Preliminary assignments of these rather complex spectra will be given, and further experiments designed to uncover possible mode specificities in the ISC process will be described.

[1]Work supported by The National Science Foundation.

[2]S. M. Beck, D. E. Powers, J. B. Hopkins, and R. E. Smalley, J. Chem. Phys. 73, 2019 (1980).

[3]F. M. Behlen and S. A. Rice, J. Chem. Phys. 75, 5672 (1981).

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MG10. (4:01)

OPTICALLY DETECTED MAGNETIC RESONANCE STUDIES OF TRIPLET CYCLOPENTANONE AND SOME OF ITS ISOTOPICALLY LABELED DERIVATIVES [1]

W. BRYAN LYNCH AND D. W. PRATT

For some time the triplet state of cyclopentanone has been known to exhibit three optically detected magnetic resonance (ODMR) spectra (triads) as opposed to the usual one. One possible explanation given for the origin of the triads is interconversion between electronic configurations, either thermally or quantum mechanically activated.[2] The most intense triad displays 'bizarre' kinetics at liquid nitrogen temperatures.[3] Phosphorescence, ODMR, PMDR, and MIDP studies of cyclopentanone and some deuterated derivatives in various media have been undertaken in our laboratory. We have found very little shift in ODMR line frequency when cyclopentanone is doped into a hydrocarbon glass matrix. Upon deuteration, the ODMR lines do shift, with the extent of shift depending upon the triad. Time resolved spectra indicate vast differences in the lifetimes of different triads. These findings will be used to build a model which can account for the origin of the triads.

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[1] Work supported by The National Science Foundation.

[2] A. L. Shain and M. Sharnoff, Chem. Phys. Lett. 22, 56 (1973).

[3] A. L. Shain and M. Sharnoff, Chem. Phys. Lett. 16, 503 (1972).

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MG11. (4:1[illegible])

Electronic Excited State Properties of Several Small Ring Compounds

D. D. Altenloh, L. Lin, L, Ashworth and B. R. Russell

Electric field studies have been made to determine certain electronic excited state properties of several small ring compounds. These properties include excited state dipole moment, excited state mean polarizability and direction of the transition moment. The electric field method utilizes intense externally applied electric fields to effect changes in the absorption profile due to orientation of polar gaseous compounds. The resulting electric field data permits determination of the properties indicated. The studies have concentrated on the lower energy Rydberg absorptions to help characterize these states in comparison to the higher energy intravalent transitions. In addition, differences in these excited state properties are noted for the s, p, and d Rydberg transitions.

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MG12. (4.35)

TWO-PHOTON EXCITATION SPECTRUM OF PERYLENE*

Y.C. CHUNG, I. SUZUKA AND G. E. LEROI

The two-photon excitation technique is being applied to fluorescent, centrosymmetric polycyclic hydrocarbons and heteronuclear aromatics. We report here TPE spectra of perylene ($C_{20}H_{12}$, *peri*-dinaphthalene), which has D_{2h} symmetry. Both A_g and B_g excited electronic states - which are "hidden" in the normal absorption spectrum - are revealed in the 250-400 nm region when $\sim 10^{-4}$M solutions of perylene in n-octane are irradiated by near infrared light from a tunable Nd:YAG-pumped dye laser. Assignments are based on the relative intensity of the two-photon induced fluorescence under linear and circular polarization of the laser source. The experimentally-determined excited state energies will be compared with published theoretical (SCF) calculations.[1]

*Research supported in part by the U. S. National Science Foundation.

[1]Y. Tanizaki, T. Yoshinaga and H. Hiratsuka, Spectrochim. Acta 34A, 205 (1978).

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MG13. (4:52)

PHOTO-THERMAL SPECTROSCOPY OF BENZENE AND PYRIDINE FILMS SUPPORTED ON METAL SURFACES.

P. GERAGHTY, M. WIXOM, A. H. FRANCIS

The electronic absorption spectra of physisorbed and chemisorbed pyridine and benzene on metal surfaces have been recorded at temperatures between 8 K and 300 K using a novel photo-thermal spectroscopy. The photo-calorimetric nature of the experiment makes possible the quantitation of absorption cross-section and the determination of surface coverage. The experimental method permits an improvement in signal recovery from noise over other techniques used in the electronic spectroscopy of surfaces and may also be employed to obtain the vibrational spectra of surface adsorbates at monolayer coverage. Additional advantages and some disadvantages of the method relative to other techniques for surface spectroscopy will be discussed.

The spectra of pyridine and benzene have been obtained on evaporated films of aluminum, silver, gold and nickel. The results may be interpreted in terms of surface structure, reorganization of the surface film, chemisorption and physisorption.

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MH1. (1:30)

FAR-INFRARED AND RESONANCE RAMAN SPECTRA OF POLYHALIDES

E. M. NOUR, L.-H. CHEN, AND J. LAANE

The far-infrared and Raman spectra of various polyhalide ions including $M^+I_3^-$, $M^+I_2Br^-$, $M^+Br_3^-$, $M^+I_5^-$, $M^+I_4Br^-$, $M^+I_7^-$, and $M^+I_9^-$ for M^+=Cs^+, $(CH_3)_4N^+$, $(C_2H_5)_4N^+$, etc. have been recorded and analyzed. The fundamental vibrational frequencies for each of the ions are below 210 cm^{-1}. The frequency patterns allow classification of the various ions according to structural units. For example, I_5^- ions may be $(I_3^-)(I_2)$ and I_9^- may be $(I_5^-)(2I_2)$.

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MH2. (1:47)

THE FAR-INFRARED TORSIONAL SPECTRUM OF METHYL SILANE

H. JAGANNATH, M. WONG* AND I. OZIER†

The torsional transitions in symmetric tops with internal rotation are known to be weak and are allowed only through vibration-torsion-rotation interactions. The torsional spectrum is here reported of methyl silane taken with Fourier transform spectroscopy in the region 150-380 cm^{-1} at a resolution of 0.15 cm^{-1}. Densities ranged from 0.36 to 0.96 amagats with a path length of 12.4 m; the sample was at room temperature. Several torsion-rotation bands from torsional levels with v = 0, 1, and 2 have been observed. Work is underway to analyse the present data along with the microwave frequencies and molecular beam splittings available to obtain the torsion-rotation constants and the parameters characterizing the transition dipole operator. Preliminary results will be reported.

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MH3. (1:5?)

VIBRATIONAL ANALYSIS AND NORMAL COORDINATE CALCULATIONS OF SOME ALKYL THIOCYANATES AND ISOTHIOCYANATES

H. L. HEUSEL, J. R. DURIG, J. F. SULLIVAN, AND S. CRADOCK

The infrared and Raman spectra of CH_3NCS, CH_3SCN, CH_3CH_2NCS and CH_3CH_2SCN, as well as CD_3NCS and CD_3CD_2NCS, have been recorded for all three phases. The vibrational spectrum of methylisothiocyanate has been interpreted in terms of a "pseudo" symmetric top molecule and assigned according to C_{3v} symmetry, whereas the methyl torsion for methylthiocyanate, assigned according to C_s symmetry, has been observed and the barrier has been calculated.

The vibrational spectra of the ethylthiocyanate and ethylisothiocyanate molecules, which can exist as a mixture of conformers, have been assigned; however, only the vibrational spectrum of the CH_3CH_2SCN molecule shows evidence of a second conformer. A variable temperature study of the Raman spectrum of liquid CH_3CH_2SCN has been carried out in the region of the C-S-C symmetric stretch, and the ΔH has been obtained.

Normal coordinate calculations have been carried out on all of these molecules. The force fields will be compared among these compounds, as well as among other thiocyanate molecules.

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MH4. (2:15)

CONFORMATIONAL BARRIERS TO INTERNAL ROTATION OF 3-FLUOROPROPENE BY FT-IR SPECTROSCOPY

T. S. LITTLE, J. R. DURIG, AND MENGZHANG ZHEN

The hindered internal rotation motion in the 3-fluoropropene molecule has been investigated through a study of the far infrared spectrum of the gas at ambient temperature using FT-IR spectroscopy. The asymmetric torsion for the cis conformer was observed at 164.6 cm^{-1} with four accompanying hot bands, and the corresponding torsion of the gauche conformer was observed at 108.4 cm^{-1} with three additional hot bands. From these data the potential function for internal rotation of the asymmetric top has been determined and the following potential constants have been evaluated: $V_2 = 403 \pm 27$, $V_3 = 815 \pm 6$, $V_4 = 42 \pm 8$, and $V_6 = -36 \pm 3$ cm^{-1}. From these data it has been determined that the cis conformer is the predominant form at ambient temperature and the enthalpy difference between the cis and gauche conformers is 126 cm^{-1} (360 cal/mol). The calculated cis-gauche barrier is 1156 cm^{-1} (3.31 kcal/mol) and the gauche-gauche and gauche-cis barriers are 496 cm^{-1} (1.42 kcal/mol) and 839 cm^{-1} (2.40 kcal/mol), respectively. These data will be discussed in relation to the corresponding information for several other similar molecules.

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MH5. (2:31)

ROTATIONAL AND VIBRATIONAL SPECTRUM OF TRANS-1-FLUORO-2-BUTENE

T. S. LITTLE, J. R. DURIG, AND MENGZHANG ZHEN

The microwave spectrum of trans-1-fluoro-2-butene has been recorded from 18.0 to 39.0 GHz. The R-branch assignments of the ground and first two excited states of the observed a-type spectrum have been made. The ground state rotational constants are: A = 18943 ± 317, B = 2071.34 ± 0.04 and C = 2022.11 ± 0.04 MHz. It is shown that these rotational constants are consistent with a gauche orientation of the CH_2F moiety. Additionally, several lines observed in the microwave spectrum could not be assigned to the gauche rotamer but, on the basis of an investigation of the infrared and Raman spectra, they have been assigned to the cis conformer. An investigation of the far infrared spectrum of trans-1-fluoro-2-butene has allowed the assignment of the asymmetric torsional mode of the cis rotamer to a series of Q-branches beginning at 123.9 cm^{-1}. These results will be compared to the corresponding quantities in similar molecules.

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MH6. (2:48)

THE VIBRATIONAL SPECTRUM AND STRUCTURE OF HEXAFLUOROACETONE

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The vibrational spectrum of gaseous hexafluoroacetone has been reexamined. The use of current Raman techniques allows the accurate observation of intensity and polarization properties of bands in the spectrum in order to identify them with molecular symmetry species. As found previously,[1] the characteristics of the spectrum are consistent with a C_{2v} molecular symmetry, in contradiction with the C_2 structure found by electron diffraction.[2]

To investigate this discrepancy, a 3-21G SCF ab initio calculation was carried out to estimate the structure and the vibrational force field. The ab initio structure was found to be C_2, in agreement with the electron diffraction result. The ab initio force field, weighted in the accepted manner, predicts vibrational frequencies which are readily identifiable with the observed spectrum. Further, it is found that, to a great extent, the symmetry coordinates which combine to make up a given normal mode all correlate with the same symmetry species under C_{2v}. Using this fact we can understand how the observed spectrum may be interpreted on the basis of C_{2v} symmetry when the actual molecular symmetry is C_2.

[1] C.V. Berney, Spectrochim. Acta 21, 1809 (1965); F.A. Miller and F.E. Kiviat, Spectrochim. Acta 25A 1577 (1969).
[2] R.L. Hilderbrandt, A.L. Andreassen and S.H. Bauer, J. Phys. Chem. 74 1586 (1970).

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MH7. (3:15)

Theoretical Study of the Conformational Properties and Torsional Potential Functions of Methacryloyl Fluoride

B. Laskowski, R. Jaffe, and A. Komornicki

The suitability of ab initio Self Consistent Field (SCF) molecular orbital and gradient methods for determining the conformational energies and torsional potentials of organic molecules such as methacryloyl fluoride (CH_2=$C(CH_3)COF$) is demonstrated.

Often the barrier heights to internal rotations are not measured directly by experiment, but determined by extrapolation. However, theory allows for a direct determination.

The two experimental studies[1,2] for methacryloyl fluoride, regarding the rotational barriers for the COF and CH_3 groups are evaluated in light of the theoretical study. In addition a normal mode analysis is made which complements the Infrared and Raman experiment of Durig and coworkers[1].

The calculations suggest that to obtain reasonable barrier heights for larger molecules it would be sufficient to use the 4-31 G basis set, to optimize, using the SCF gradient method, the geometries of the conformations corresponding to local minima and between those, perform SCF calculations following a path of geometrical positions obtained by interpolation.

[1] J.R. Durig, P. A. Brletic and J. S. Church, J. Chem. Phys. 76, 1723 (1982)

[2] L. A. Glebova, A. V. Abramenkov, L. N. Margolin, A. A. Zenkin, Yu A. Pentin and V. I. Tyulin, Zh. Strukt. Khim. 20, 1030(1979)

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MH8. (3:27)

VIBRATIONAL SPECTRA AND CONFORMATIONS OF (CYANOMETHYL)CYCLOPROPANE AND DICYCLOPROPYLMETHANE

V.F. KALASINSKY, J.L. POOL, Y.Y. YEH, and C.J. WURREY

The infrared and Raman spectra of (cyanomethyl)cyclopropane and dicyclopropylmethane have been studied. Each molecule exhibits a conformational equilibrium in the fluid states while a single conformer exists in the crystalline solid state. Two sets of doublets exist in the Raman spectrum of liquid (cyanomethyl)cyclopropane and the temperature dependence of the line intensities is consistent with an energy difference of 0.70 ± 0.10 kcal/mole with the gauche conformer more stable than the cis. In dicyclopropylmethane, at least two conformers exist in the liquid state, and these have been identified as gauche-gauche conformers exhibiting C_2 and C_s molecular symmetries. The former was determined to be 0.93 ± 0.10 kcal/mole more stable than the latter. Comparisons with similar molecules and a discussion of the conformer equilibria will be given.

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MH9. (3:42)

VIBRATIONAL SPECTRA AND CONFORMATIONS OF (IODOMETHYL)CYCLOPROPANE DERIVATIVES

V.F. KALASINSKY, Y.Y. YEH, and C.J. WURREY

The infrared and Raman spectra of (iodomethyl)cyclopropane and epiiodohydrin have been studied in the fluid and solid phases. (Iodomethyl)cyclopropane exists in a gauche conformation, and no evidence of a second conformer was found. Epiiodohydrin (iodomethyloxirane) has been found to exist as at least two conformations in the liquid state. The gauche-1 and gauche-2 conformations are separated by 0.50 ± 0.10 kcal/mole with the former being the more stable. In the solid state, the Raman spectrum exhibits bands for the gauche-1 conformer, but previously reported infrared spectra indicate that either form may exist in the solid state. The conformational equilibria in this molecule and its relationship to the other epihalohydrins will be discussed.

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MH10. (3:54)

VIBRATIONAL SPECTRA AND CONFORMATIONS OF 2-FLUOROETHYLAMINE

J.A. SMITH AND V.F. KALASINSKY

The infrared and Raman spectra of 2-fluoroethylamine have been recorded for the fluid and solid phases and in solution. The temperature dependence of line intensities in the liquid state and the differences between the spectra of the liquid and solid indicate that at least two conformers exist in the liquid state. There is also evidence that the extent of hydrogen bonding is different for the two conformers which have been identified. Moderately high resolution infrared spectra of the vapor exhibit rather complicated rotational and hot-band structured as well as multiplets which are attributable to multiple conformations. The gauche-trans and gauche-gauche conformers have tentatively been identified, and the structures will be discussed in terms of the intra- and intermolecular forces which are operative.

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MH11. (4:11)

EVIDENCE FOR ANHARMONIC SKELETAL DEFORMATIONS IN A SERIES OF BICYCLO[2.2.1]HEPTANES AND BICYCLO [3.2.1]OCTANES

H. WIESER, N. IBRAHIM, T.L. SMITHSON, AND P. J. KRUEGER

The far-infrared spectra in the region of 50-400 cm^{-1} are reported for several oxygen, carbonyl, exocyclic methylene, and methyl substituted analogs of bicyclo[2.2.1]heptane and bicyclo [3.2.1]octane in the vapor phase. All compounds exhibit one or more absorptions that show characteristics Q-branch sequences. These are interpreted as arising from anharmonic deformations of the bicyclic rings. The implications for the molecular structures and conformations are discussed.

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MH12. (4:28)

FT-FAR INFRARED VAPOR PHASE SPECTRA AND INVERSION BARRIERS OF A SERIES OF CYCLOHEXANE AND CYCLOHEXENE DERIVATIVES

H. WIESER, N. IBRAHIM, T. L. SMITHSON, AND P. J. KRUEGER

The far-infrared spectra in the region of 50-450 cm^{-1} have been recorded for a large variety of cyclohexane and cyclohexene derivatives in the vapor phase. The spectra exhibit one or more typical sequences of Q branches characteristic of low energy anharmonic skeletal deformations. From the positions of the appropriate sequences, barriers to planarity are estimated, and in some cases where no structural information is available from other sources the likely form of the most stable conformation is suggested. Molecules used to demonstrate the work include 3,6-dihydro-2H-pyran, 3,6-dihydro-2H-thiopyran, 3-methylene and 4-methylene cyclohexene, 3-cyclohexen-1-one, cyclohexanone, tetrahydro-4H-pyran-4-one, tetrahydro-4H-pyran-2-one, and 1,3-dioxan-5-one.

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MH13. (4:45)

A COMPARISON OF APPROACHES FOR SOLUTIONS TO THE COUPLED TWO-DIMENSIONAL ANHARMONIC OSCILLATOR

T. L. SMITHSON, H. WIESER, R. PAUL, AND F. W. BIRSS

Experience indicates that the bend/twist skeletal deformations of a number of 5- and 6-membered ring compounds should be described in terms of a coupled two-dimensional anharmonic oscillator (1). In the past, two slightly different variational approaches have been used to obtain the required solution, one using as basis the two-dimensional isotropic harmonic oscillator functions (2,4), the other the direct product formed from the one-dimensional anharmonic oscillator functions (3,4). We have explored alternative methods for obtaining the solutions, namely one using the Rayleigh-Schrödinger perturbation theory with Padé approximants, and one SCF- like modification of the variational product basis set approach. The abilities of all the methods for solving the Hamiltonian are compared for a number of molecular systems. Some of the problems associated with the methods are discussed in the context of highly coupled vibrations.

(1) L. A. Carreira, R. C. Lord, and T. B. Malloy, Jr., in "Topics in Current Chemistry", vol. 82, Springer-Verlag (1979).
(2) L. A. Carreira, I. M. Mills, and W. B. Person, J. Chem. Phys. 56, 1444 (1972).
(3) T. Ikeda and R. C. Lord, J. Chem. Phys. 56, 4450 (1972).
(4) L. E. Bauman, P. M. Killough, J. M. Cooke, J. R. Villarreal, and J. Laane, J. Phys. Chem. 86, 2000 (1982).

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TA1. (8:30)

HETERODYNE FREQUENCY MEASUREMENTS FOR INFRARED CALIBRATION TABLES; CO, N_2O, OCS, ETC.*

C. R. POLLOCK, F. R. PETERSEN, D. A. JENNINGS, J. S. WELLS, AND A. G. MAKI

By using a color center laser or a tunable diode laser, we have made accurate frequency measurements on the 2-0 band of CO, the 00^02-00^00, 20^01-00^00 and 12^01-00^00 bands of N_2O, and many bands of OCS. All measurements have been made by locking the laser to the absorption maximum of the line to be measured and then measuring the frequency difference between the tunable laser and appropriate harmonics or combinations of one or two CO_2 lasers. In some cases the tunable laser frequency was measured against a CO laser which was in turn measured against combinations of two CO_2 laser frequencies.

In keeping with infrared calibration tradition, the 2-0 absorption band of CO has been measured with the greatest accuracy. Saturated absorption measurements with a line-width of about 3 MHz have made it possible to measure the CO absorption frequencies with an absolute accuracy of about 100 kHz (0.000004 cm^{-1}). The importance of the pressure shift of the absorption frequencies will be discussed. An atlas of accurate OCS absorption frequencies will also be described.

*This work was supported in part by the NASA Upper Atmosphere Research Office.

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TA2. (8:52)

HIGH RESOLUTION INFRARED SPECTRA OF HIGH TEMPERATURE DIATOMICS

A. G. MAKI AND F. J. LOVAS

A tunable diode laser has been used to measure the spectra of a number of molecules that are difficult to observe in the gas phase at room temperature. Measurements have been made on KF, LiF, SnO, PbS, and other species that absorb between 828 cm^{-1} and 880 cm^{-1}. Temperatures between 1000 K and 1425K were used. Either $\Delta v=1$ or $\Delta v=2$ transitions were observed, depending on the match between the molecular vibrational frequency and the available diode laser element. The spectra were fit directly to a Dunham potential function by means of a non-linear least-squares program. A single potential function with a mass dependent B_e and ω_e has been used to fit the spectra for several isotopic species.

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TA3. (9:09)

DIFFERENCE FREQUENCY LASER SPECTROSCOPY OF OD AND OH: SIMULTANEOUS FIT OF THE INFRARED AND MICROWAVE LINES

T. AMANO

The infrared fundamental band ($v = 1 \leftarrow 0$) of OD has been observed with a tunable difference frequency laser. The corresponding band of OH has also been observed with higher accuracy than in a previous emission measurement.[1] Simultaneous fits of the infrared and microwave data are made to obtain improved molecular constants. The band origin and the rotational constants are (in cm^{-1}):

	ν_0	$\tilde{B}_0$	$\tilde{B}_1$
OD	2632.06118(28)	9.877664(38)	9.602134(28)
OH	3569.6348(30)	18.53053(12)	17.81987(12)

[1]J.P. Maillard et al., J. Mol. Spectrosc. 63, 120 (1976).

TA4. (9.21)

EXPERIMENTAL DETERMINATION TO LARGE INTERNUCLEAR SEPARATION OF THE $^1\Sigma^+$ STATE ELECTRIC DIPOLE MOMENT FUNCTION OF CO

C. CHACKERIAN, JR., R. FARRENQ, G. GUELACHVILI, C. ROSSETTI, AND W. URBAN

We have experimentally determined the EDMF of CO's ground electronic state to about the classical turning points of the V=40th level. The Pade' approximant representation of the EDMF is determined via a non-linear least-squares fit which combines numerically obtained vibrational wavefunctions and experimentally determined vibrational band intensities for which Δv = 1, 2, 3 and 40 for both $^{12}C^{16}O$ and $^{13}C^{16}O$. The experimental intensities were obtained from plasma emission spectra by considering pairs of vibrational transitions from common upper vibrational states and assuming a well defined rotational temperature. These results should be useful in the interpretation of solar infrared spectra.

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TA5. (9:38)

FAR-INFRARED LASER MAGNETIC RESONANCE SPECTROSCOPY OF THE PD($^3\Sigma^-$) RADICAL

N. OHASHI, K. KAWAGUCHI, AND E. HIROTA

In this work we report the results on the pure rotational spectra of the PD($^3\Sigma^-$) radical obtained by using far-infrared laser magnetic resonance (FIR LMR) spectroscopy.

The FIR LMR spectrometer used in the present work has recently been constructed at the Institute for Molecular Science. The design of the FIR laser is similar to that described by Evenson.[1]

The PD radical was generated by passing microwave discharged D_2O or D_2 gas over red phosphorus powder at 200 mT pressure.

The FIR LMR spectra of PD were recorded with the laser lines of 570μm, 380μm, 287μm, 232μm, 191μm and 164μm for the v = 0 state, and 392μm for the v = 1 state. The doublet hyperfine splittings due to the P nucleus were well resolved in all the observed spectra. The triplet hyperfine splitting due to the D nucleus was observed only for N,J = 3,2 ← 2,1 transition. Combining the present FIR LMR data with the IR LMR data obtained by Uehara and Hakuta[2], the molecular constants of the PD($^3\Sigma^-$) radical were refined, for example, B"=4.362877(16)cm^{-1}, λ"=2.20829(74)cm^{-1}, B'=4.269241(59)cm^{-1} and λ'=2.2090(14)cm^{-1}.

We also observed the pure rotational spectra of the PO_2 and PO radicals in the reaction of microwave discharged D_2O and red phosphorus. We report briefly their spectra and the reaction mechanism for generating these radicals.

[1]K. M. Evenson, Faraday Discuss., Chem. Soc. 71, 7 (1981).
[2]H. Uehara and K. Hakuta, J. Chem. Phys. 74, 4326 (1981).

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TA6. (10:05)

OBSERVATION OF INFRARED SiH in a SiH_4 PLASMA

P. CHOLLET, G. GUELACHVILI, M. MORILLON and
P. GRESSIER, G. de ROSNY, J. SCHMITT

A preliminary experiment of high resolution absorption and emission spectroscopy of a silane plasma in the 1800-2300 cm^{-1} range has been previously reported 1 . The detection of the 1-0 band of the free radical SiH, at 2000 cm^{-1} was then obtained with a poor signal-to-noise ratio. In order to increase the sensitivity of the detection a new experimental set-up has been built. The SiH_4 plasma is observed in a 2.5 m long source containing a White-type multi-reflexion system. The spectra are recorded with the Fourier transform interferometer of Laboratoire d'Infrarouge, with a simultaneous control of the conditions of the excitation of the plasma. Description of the experimental system, and preliminary results are given.

[1]J.C. Knights, J.P.M. Schmitt, J. Perrin and G. Guelachvili, J. Chem. Phys., 76, p.3414-3421 (1982).

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TA7. (10:22)

DIPOLE MOMENT OF THE FO RADICAL

A.R.W. McKELLAR

It has long been a puzzle why the FO radical could not be detected by means of microwave or gas phase electron resonance spectroscopy even after extensive study of the related group VI-VII diatomics (ClO, BrO, SF, SeF, etc.) The recent observation[1] of a strong vibrational spectrum of FO using laser magnetic resonance (LMR) demonstrated that production of the radical in the gas phase was not especially difficult, and suggested that a small permanent dipole moment might be responsible for the absence of rotational or EPR data.

By applying a moderate (~1 kV/cm) electric field while observing saturated absorption signals in the LMR spectrum at 9.7 μm, it has now been possible to measure the dipole moment. The values obtained are amazingly small (e.g. 0.0026 D for v=0, J=1.5; 0.024 D for v=1, J=1.5) and they fully explain the previous lack of success in observing spectra in the microwave region.

[1]A.R.W. McKellar, Can. J. Phys. 57, 2106-2113 (1979).

Address of McKellar: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada.

TA8. (10:39)

OBSERVATION OF THE ν_1 BAND OF DO_2 BY DIFFERENCE FREQUENCY SPECTROSCOPY

K. G. LUBIC AND T. AMANO

The ν_1 fundamental band of DO_2 was observed using a tunable infra-red difference frequency laser. DO_2 was generated by an a.c. discharge in CH_3OD and O_2 at a total pressure of 1 torr in a multipass, Zeeman-modulated cell. The rotational-vibrational lines, which occurred near 3.9 μm (2550 cm^{-1}), were analyzed and molecular constants were determined by a least squares fit.

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TA9. (10:56)

DETECTION OF THE ν_2 BANDS OF CD_2 AND CH_2 BY INFRARED DIODE LASER SPECTROSCOPY

A.R.W. McKELLAR, CHIKASHI YAMADA, AND EIZI HIROTA

Using a tunable diode laser spectrometer with a Zeeman-modulated multiple-reflection cell, we have observed five transitions of CD_2 around 710 cm^{-1} and two of CH_2 around 892 cm^{-1}. One of the CH_2 transitions ($4_{13} \leftarrow 4_{22}$) represents a new measurement, and the other ($4_{04} \leftarrow 4_{13}$) had been observed previously by laser magnetic resonance.[1]

The CD_2 transitions were of the form $N_{0,N} \leftarrow N_{1,N-1}$ with $N = 3$ to 7. They represent the first observation of ν_2 in CD_2, and the lines were found just 1.5 cm^{-1} higher than predicted by a nonrigid bender analysis[2] of CH_2 data. The present results yield the ν_2 band origin for CD_2 (752.375 cm^{-1}) as well as $\frac{1}{2}(B+C)$, Δ_N, and D (the diagonal spin-spin interaction parameter) for the $v_2 = 1$ state.

[1] T.J. Sears, P.R. Bunker, and A.R.W. McKellar, J. Chem. Phys. 77, 5363 (1982).
[2] P. Jensen, P.R. Bunker, and A.R. Hoy, J. Chem. Phys. 77, 5370 (1982).

Address of McKellar: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada.
Address of Yamada and Hirota: Institute for Molecular Science, Okazaki 444, Japan.

TA10. (11:13)

LASER MAGNETIC RESONANCE OF GERMANIUM CONTAINING SPECIES

T.J. SEARS, A.R.W. McKELLAR, AND M. WONG

We have observed extensive laser magnetic resonance spectra in the 880 to 950 cm^{-1} region resulting from the reaction of GeH_4 with F atoms from a microwave discharge in CF_4. A few relatively weak lines have been assigned to the $^2\Pi_{1/2} \leftarrow {}^2\Pi_{3/2}$ transition of GeH, but one or more other molecules are responsible for most of the observations. The presence of Ge in the carrier(s) of the spectra is confirmed by experiments with isotopically pure $^{74}GeH_4$. The most likely candidate molecule is GeH_3, and we have made some tentative rotational assignments on this basis. However, a rapid analysis of the spectra is retarded by the absence of any previous data on gas phase GeH_3, by the presence of a number of Ge isotopes, and by the fact that two vibrational fundamentals (ν_2 and ν_4) occur in this region which are likely to be Coriolis-coupled (moreover, ν_4 is degenerate). Other molecules which could possibly be involved in our observations are GeH_2F, GeF, or excited $^3B_1$ GeH_2.

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TA11. (11:30)

OBSERVATION OF ν_2 FCO WITH CO_2 LASER MAGNETIC RESONANCE

W. J. McCOY, R. E. MUENCHAUSEN, AND G. W. HILLS

The laser magnetic resonance spectrum of the ν_2 band of FCO has been observed throughout the region from 1040-1090cm^{-1}. The FCO was produced in the reaction of F+CO+Ar, where the F atoms are produced in a microwave discharge in either CF_4+Ar or SF_6+Ar. FCO is also present in "pure CF_4" discharges, in which the necessary O atoms are apparently derived from the quartz cell walls. The majority of resonances occurred at low field (<2kG), but a few high field lines, including some with an uncharacteristic shape, were observed. Several lines exhibit clearly resolved doublet structure, most likely due to ^{19}F hyperfine effects. In the previous diode laser study[1], only a-type transitions were assigned. In contrast, our preliminary analysis indicates that both a- and b- type transitions occur in the LMR spectrum.

[1]K. Nagai, C. Yamada, Y Endo and E. Hirota, J. Mol. Spectrosc., 90, 249 (1981).

Address: Department of Chemistry, The University of North Carolina, Chapel Hill, N.C. 27514

TA12. (11:47)

HIGH RESOLUTION FOURIER TRANSFORM SPECTROSCOPY OF THE ν_2 AND ν_3 BANDS OF FNO

S.C. FOSTER AND J.W.C. JOHNS

The bending (519.6 cm^{-1}) and NF stretching (765.4 cm^{-1}) fundamental vibrations of nitrosyl fluoride have been recorded with a BOMEM model DA3.002 Fourier transform spectrometer at a resolution of $\sim$0.004 cm^{-1}. Data from the present analysis have been combined with available microwave data to provide optimum molecular constants for the 000, 010 and 001 states of FNO.

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TB1. (8:30)

THE LOW LYING ELECTRONIC STATES OF CeO, PrO, EuO, and YbO

M. DULICK, R.F. BARROW, C. LINTON, S. MC DONALD, S. RICE, AND R.W. FIELD

The lowest energy electronic states of CeO and PrO are found to arise from fs and f^2s free M^{2+}-ion configurations perturbed by an O^{2-} ligand. EuO and YbO are unique among the lanthanide oxides in that their lowest electronic configuration is f^N rather than $f^{N-1}s$. An $^9\Sigma^-$ - $^8\Sigma^-$ transition of EuO has been partially analyzed.

In order to evolve and test a Ligand Field model for the electronic structure of the LnX and LnX^+ (X = O,S,H,F,Cl,Br,I) molecules, certain critical energy level splitting must be observed.

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Address of Linton, Department of Physics, University of New Brunswick, Fredericton, N.B. CANADA.

TB2. (8:47)

ENERGY LINKAGE OF THE SINGLET AND TRIPLET MANIFOLDS IN LaF

H. SCHALL, R.W. FIELD, AND C. LINTON

A combination of dispersed laser induced fluorescence and Doppler-limited fluorescence excitation spectroscopy has been used to examine the electronic spectrum of the LaF molecule. Dispersed fluorescence experiments have located the $a_1\ {}^3\Delta_1$ state at $T_0 = 1432 \pm 2\ cm^{-1}$ above the $X^1\Sigma^+$ state. In addition, two $\Omega = 2$ levels are found at $T_0 = 1790 \pm 2$ ($a_2\ {}^3\Delta_2$) and $5460 \pm 2\ cm^{-1}$. A new $0^+ - X^1\Sigma^+$ transition was observed with $T_0 = 16637.95\ cm^{-1}$ and $B_0 = 0.2303\ cm^{-1}$.

The results of these initial experiments will be reported and the energy level diagram will be discussed in terms of Ligand Field Theory.

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TB3. (9:04)

THE LOW LYING ELECTRONIC STATES OF HOLMIUM OXIDE

Y.C. LIU, H. SCHALL, R.W. FIELD, AND C. LINTON

Laser spectroscopic techniques have been used to probe the structure of the Holmium Oxide (HoO) molecule. Resolved fluorescence has been used to determine energy linkages between electronic states. High resolution excitation spectroscopy was used to observe rotational and, in some cases, hyperfine structure.

Several different transitions have been excited and rotationally analyzed. Of these, some show very large, well resolved hyperfine structure (I = 3.5 for Ho and each rotational line has 8 components). An energy diagram will be presented showing the linkages between and assignment of the low lying states, together with results of the rotational and hyperfine analysis. The assignment of the ground state, the energy order of the low lying states, and hyperfine structure will all be discussed in relation to predictions of Ligand Field Theory.

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TB4. (9:21)

THE ELECTRONIC STRUCTURE OF THE LnX AND LnX^+ (X = O,H,F,Cl,Br,I) MOLECULES

S.F. RICE, M. DULICK, AND R.W. FIELD

A Ligand Field based semiempirical model for the description of the electronic structure of the low lying states of Rare Earth halides, hydrides, and oxides will be presented. The theory leads to an ordering of ionic molecular configurations corresponding to groups of states characterized by "large" and "small" orbitals. These configurations, composed of many states, are shown to be directly related to the states of the free ion, Ln^{n+}. Spectroscopic constants such as vibrational frequencies, bond lengths, and hyperfine splittings, as well as symmetry and position of energy levels of the few molecules of this class that have been studied will be compared to the predictions of the theory.

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TB5. (9:38)

IMPROVED VIBRATIONAL CONSTANTS OF ScO, YO AND LaO

CARLOS B. SUAREZ

We report a new set of improved vibrational constants for ScO, YO and LaO and some additional figures for these species. The idea has been to fill the lack of sufficient and suitable constants needed to define the potential-well necessary in some calculations where they are the main limitation, as in Franck-Condon factors for instance. In order to do this, unreliable head measurements and little available band origins are ruled out, taking into account only resolved rotational structure, even if fragmentary. The accuracy of the constants is very much increased. Test of the potential-well is done reobtaining known rotational constants, and for further consistency numerical calculation of centrifugal distortion constants is performed and comparison shows agreement with experimental data.

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TB6. (10:10)

CURRENT WORK ON THE ANALYSIS OF THE CHEMILUMINESCENCE FROM LEAD OXIDE, E. A. DORKO, J. W. GLESSNER AND L. L. RUTGER

The flow tube and burner used to generate a chemiluminescent flame of lead oxide (PbO) have been redesigned in order to enhance the emission from the flame. A 0.5 m Jarrel-Ash monochromator was used with an RCA 7265 photomultiplier tube to resolve the emission. Flame temperature as measured with a thermocouple was 175°C. On the basis of a mass balance the upper limit of the number density of lead atoms was calculated to be 2×10^{14} atoms/cc for a crucible temperature of 890°C.

Lead oxide spectra were observed over the range 400-750 nm. The resolution for intense spectral regions was 2.5 Å. Emissions were observed for the band systems D—X, B—X, A—X, b—X, and a—X. A linear least squares program was written to calculate the spectroscopic constants for each of the states. The program which used a weighted average over all data was based on a procedure initially developed by Albritton and co-workers(1). Potential energy curves were prepared for some of the energy states with a program developed by C. Vidal and co-workers(2) which utilized the RKR and inverted perturbation approach (IPA). Results for PbO will be presented and discussed.

[1] D. L. Albritton, A. L. Schmeltekopf, and R. N. Zare, J. Mol. Spectrosc. 67, 132 (1977).

[2] C. R. Vidal and H. Scheingraber, J. Mol. Spectrosc. 65, 46 (1977).

Address: Dept of Engineering Physics, Air Force Institute of Technology, Wright-Patterson AF Base, Ohio, 45433.

TB7. (10:27)

A ROTATIONAL ANALYSIS OF THE C $^1\Pi$ - X $^1\Sigma^+$ SYSTEM OF InCl

S. KING, W.B. GRIFFITH, C.W. MATHEWS

The absorption spectrum of the C $^1\Pi$ - X $^1\Sigma^+$ system of InCl has been recorded in the region 2650 - 2800 Å. Our spectrum is in good agreement with that reported by Froslie and Winans[1] except that our resolution is appreciably higher. The improved resolution in the present study along with the availability of precise microwave data[2-4] for the ground state permits us to obtain significantly improved constants for the v=0 level of the C $^1\Pi$ state. As has been previously noted, levels with v'>0 become progressively diffuse indicating predissociation. Predissociation in bands involving v'=0 is indicated by increasing line width with increasing J.

[1] H.M. Froslie, J.G. Winans, Phys. Rev. 72, 481 (1947)
[2] A.H. Barrett, M. Mandel, Phys. Rev. 109, 1572 (1958)
[3] J. Hoeft, Z. Phys. 163, 262 (1961)
[4] G.A.L. Delvigne, H.W. de Wijn, J. Chem. Phys. 45, 3318 (1966)

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TB8. (10:39)

VIBRATIONAL AND ROTATIONAL ANALYSIS OF HIGH LYING VIBRATIONAL BANDS OF THE BaO A' Σ^+ AND A' $^1\Sigma$ STATES

NICK FURIO AND J. GARY PRUETT

Vibrational levels V=10 through V=18 of the BaO excited singlet states are analyzed and their perturbations with nearby states are determined in order to search for unusual perturbations due to $^1\Delta$ states or the ground $^1\Sigma$ state.

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TB9. (10:56)

SPARSE MAPPING OF HIGH LYING EXCITED ELECTRONIC STATES IN BaO

YEN CHU HSU AND J. GARY PRUETT

Several new excited electronic vibrational levels are observed in BaO using optical-optical double resonance via the $A'\ ^1\pi$ state. Many states of primarily $^1\Sigma$ or $\Omega=0$ character are observed as well as at least one state of $^1\pi$ or $\Omega=1$ character.

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TB10. (11:13)

FOURIER TRANSFORM INFRA-RED SPECTRUM OF CrO NEAR 8000 CM^{-1}

A. S-C. CHEUNG, A. J. MERER AND W. ŻYRNICKI

The discharge emission spectrum of CrO has been investigated with high resolution Fourier transform spectroscopy in the region 6000 - 12000 cm^{-1}. Complicated groups of bands occur in the region 7000 - 10000 cm^{-1}, of which one, near 8000 cm^{-1}, has been identified as the (0,0) band of a new $^5\Sigma$ - $X^5\Pi_r$ transition of CrO. The perpendicular polarization of this transition permits a direct determination of the Λ-doubling parameters and the spin-orbit coupling constants of the ground state, which was not possible from the analysis of the $^5\Pi$-$^5\Pi$ transition in the visible region.[1]

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[1]W. H. Hocking, A. J. Merer, D. J. Milton, W. E. Jones and G. Krishnamurty, Canad. J. Phys, 58, 516 (1980).

Address: Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, B. C., Canada, V6T 1Y6.

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TB11. (11.30)

LASER SPECTROSCOPY OF THE $^1A''$-$\tilde{X}^1A'$ SYSTEM OF CuOH AND CuOD

MITCHELL TRKULA AND DAVID O. HARRIS

The green bands of CuOH and CuOD have been studied by chemiluminescence and laser-excitation spectroscopies. CuOH and CuOD were produced by means of a recently developed hollow-cathode sputtering source. The transitions probed by laser-excitation spectroscopy were found to arise from the (0,0,0)-(0,0,0) band of a $^1A''$-$\tilde{X}^1A'$ electronic transition. The rotational analyses of the (1,0) and (0,1) rotational subbands of this system is presented. The molecules are well described as near prolate assymmetric rotors and are bent in both the ground and excited electronic states with bond angles of 111(1)° and 119(1)°, respectively.

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TB12. (11:47)

MAGNETIC ROTATION SPECTROSCOPY OF SINGLET METHYLENE

H. PETEK, D. J. NESBITT, AND C. B. MOORE

The Doppler-limited spectra of singlet methylene ($\tilde{b}\ ^1B_1 \leftarrow \tilde{a}\ ^1A_1$), have been observed by direct absorption and magnetic rotation spectroscopy (MRS). Since magnetic rotation is exhibited only by singlet methylene states that are coupled to the triplet manifold, this technique is extremely sensitive to even weak singlet-triplet perturbations. The magnetic activity is observed in greater than 80% of transitions (studied between 16000 cm^{-1} and 17000 cm^{-1}) indicating strong coupling between singlet and triplet manifolds. Large magnetic effects are observed in vibronic transitions originating from 7_{16}, 4_{31}, and 4_{32} levels, in good agreement with perturbation analysis of triplet methylene rotational LMR spectra.[1]

This work will lead to a better understanding of electronic structure of methylene and a more accurate determination of the singlet-triplet splitting, as well as a re-evaluation of the $\tilde{b}\ ^1B_1 \leftarrow \tilde{a}\ ^1A_1$ spectrum.

[1] T. J. Sears, private communication.

Address of Petek, Nesbitt, and Moore: Department of Chemistry, University of California, Berkeley, California 94720

TC1. (8:30)

THEORETICAL STUDIES ON THE ENERGY LEVEL DIAGRAM OF THE CHLOROPHYLL a DIMER

L.V. Haley, and J.A. Koningstein*

In this communication we discuss part of the energy level of dimeric Chlorophyll a and the way it relates to the absorption, fluorescence and Raman spectrum. The energy level diagram is based on the occupation of molecular orbitals of the dimer which arise if interaction occurs between highest occupied and lowest unoccupied orbitals of the monomer. The resulting dimeric energy level diagram is compared with that of the monomers and electronic Raman selection rules as well as lifetimes of excited states are discussed.

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L.V. Haley and J.A. Koningstein, Can. J. Chem. to be published (Jan. 1983).

TC2. (8:47)

EXCITED STATE AND VIBRATIONAL GROUND STATE STUDIES OF CAROTENES AND CHLOROPHYLL MONOMERS AND DIMERS

A. de Wilton, L.V. Haley and J.A. Koningstein*

Using a nanosecond tunable pulsed laser we have obtained the vibrational Raman spectrum of short lived excited states of all trans β-carotene and dimers of dry Chlorophyll a in hexane. The position of Raman shifts of the S_1 state of all trans β-carotene which has a lifetime of 265fs, is determined by applying the technique of time resolved Raman spectroscopy and our data suggest that only small differences exist in the frequencies of corresponding modes of S_1 and the S_0 ground state. A high resolution study of the Raman excitation profile of a normal mode of trans β-carotene suggest the presence of another electronic state and Raman spectrum from this state too was recorded.

Excited level Raman spectroscopic studies were also made of a solution of dry Chl a in hexane, where the majority species is the Chl a dimer. We report the first observation of hole burning in the Raman excitation profile of normal modes in the ground state from the dimer. This phenomenon is explained in terms of ground state bleaching and the occurrence of Raman scattering from exciton levels of the dimer at 14800 cm^{-1} and 16300 cm^{-1}.

*Department of Chemistry, Carleton University, Ottawa K1S 5B6, Ont. Canada.

TC3. (9.20)

TIME RESOLVED AND FREQUENCY SELECTIVE FLUORESCENCE OF THE CHL a DIMER

A. de Wilton and J.A. Koningstein*

The pulsed laser induced fluorescence of solutions of Chlorophyll a is reported. The assignment[1] of the fluorescence in terms of contribution of that of monomers, dimers and higher aggregates is discussed. The assignment is based on time resolved fluorescence spectral results in combination with the wavelength selective excitation of fluorescence of primarily the dimeric species. Quenching of this fluorescence, observed at high laser power, is observed and a discussion of this effect is given in terms of our present knowledge of the energy level scheme of the dimer in relation to that of the monomer. Energy gaps of the lowest lying exciton states of dimeric Chl a in CCl_4, hexane and benzene is reported.

*Department of Chemistry, Carleton University, Ottawa K1S 5B6, Canada
1) A. de Wilton and J.A. Koningstein, J. Phys. Chem. to be published (Jan. 1983)

TC'1. (9:55)

PHOTOACOUSTIC STUDY OF VIBRATIONAL OVERTONES IN POLYATOMIC MOLECULES.

HOWARD. L. FANG, DONNA M. MEISTER, AND ROBERT L. SWOFFORD

Intracavity gas phase photoacoustic spectroscopy is used to investigate the near-IR and visible overtone spectra of various polyatomic molecules. This report summarizes some of our current data. The description of overtone structure is based on the local mode model. It is known that the influence of the conformational environment on the X-H oscillators (X=C,O,N) can be easily observed in the overtone spectra for the X-H stretching vibration. This sensitivity to molecular geometry may provide important new information concerning the molecular conformation. Several examples are demonstrated here: (1) nonequivalent C-H bonds present in alkenes and dienes, (2) different O-H and N-H stretching vibrations in alcohols and amines, (3) nonequivalent stretching frequencies of the axial and equatorial C-H bonds in p-dioxane.

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TC'2. (10:12)

PHOTOACOUSTIC SPECTROSCOPY OF NON-EQUIVALENT METHYL C-H OVERTONE VIBRATIONS.

HOWARD L. FANG, D.M. MEISTER, AND ROBERT L. SWOFFORD

Recently considerable interest has been focussed on the success of the local mode model for describing the highly excited vibrational overtones of molecules containing X-H bonds (X=C,O,N). The development of sensitive photothermal techniques has significantly enhanced the amount of available information regarding the overtone structures in the near-IR and visible spectral region. In this report, we present the observation of non-equivalent methyl C-H bonds in four types of anisotropic environments:

(a) equatorial-axial C-H bonds (such as in iso-butane and t-butanol),

(b) the adjacent lone-pair electron moiety (such as in dimethyl ether, dimethyl sulfide and methyl amines),

(c) the adjacent C=C π-electron moiety (such as in propylene and 2-alkenes), and

(d) the adjacent C=O π-electron moiety (such as in acetaldehyde and acetone).

In all cases, two distinct C-H stretching overtone bands are observed which correspond to two types of C-H bonds in the methyl group. A MO analysis which will be described in the next paper suggests that the lone-pair or π-orbital delocalization is responsible for the appearance of two methyl C-H bands at each overtone even if the methyl group is freely rotating.

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TC'3. (10:29)

α-METHYL C-H BOND STRENGTH: A MO ANALYSIS.

A.B. ANDERSON, D. GERVASIO, H.L. FANG, D.M. MEISTER, AND R.L. SWOFFORD

We have carried out full structure determinations on several small hydrocarbon molecules with methyl groups using the ASED-MO method. Methyl rotational conformations are found to match experimental observations. α-methyl C-H bonding was studied for each of the molecules. A correlation has been found between the radical energy level position of the unrelaxed fragment and the C-H bond strength as determined by overtone vibrational studies of Fang, et al. This correlation can be understood using a perturbation argument.

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TC'4. (10:46)

PHOTOACOUSTIC STUDY OF OVERTONE STRUCTURE OF METHANOL AND METHANOL-OD

HOWARD L. FANG, D.M. MEISTER, AND ROBERT L. SWOFFORD

We report here the study of the visible and near-IR absorption of gaseous CH_3OH and CH_3OD measured with intracavity cw dye laser photoacoustic spectroscopy. The spectra show progressions of transitions for O-H, O-D and C-H stretches. Combinations involving the stretching vibrations with other vibrations are also observed between consecutive overtones. By careful comparison with the overtone spectrum of CH_3OD, the combination bands associated with the O-H stretching local modes can be identified. Six local-normal combinations, four of the combinations associated with O-H stretching and two associated with C-H stretching local modes, are observed between consecutive ΔV_{OH} overtones. These four O-H related combinations are C-O stretch (ν_{CO}), O-H bend (δ_{OH}), $\nu_{CO} + \delta_{OH}$, and the second harmonic ($2\delta_{OH}$) of the O-H bend. The two C-H related combinations are C-H bend (δ_{CH}) modes. The spectra are described in terms of a simple three coordinate local mode model which will be presented in the next paper. The systematic study of overtones helps us understand the factors which influence the potential energy surface and the potential chemical reactivity of individual X-H bonds.

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TC'5. (11:03)

COMBINATION BANDS IN THE O-H OVERTONE SPECTRA OF METHANOL: THEORY*

MARTIN L. SAGE

The observed† absorption spectra of methanol in the region of the O-H stretching overtones shows combination bands involving the O-H stretch and the H-O-C bend or the C-O stretch. A simple three coordinate model involving an anharmonic O-H stretch and harmonic H-O-C bend and C-O stretch coupled through G-matrix elements and potential constants accounts for the observed spectra.

*Supported in part by the Standard Oil COmpany (Ohio)

†H.L. Fang, preceeding abstract.

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TC'6. (11:20)

THE VISIBLE PHOTOACOUSTIC SPECTRA OF VAPOR-PHASE METHANE AND DEUTERATED METHANES AT 77 K

G. J. SCHERER, K. K. LEHMANN, AND W. KLEMPERER

We have constructed a longitudinally resonant photoacoustic cell which can be cooled to liquid nitrogen temperature. This cell has been used intracavity in our automated dye laser spectrometer[1] to obtain low temperature, Doppler-limited spectra in the visible. Working at 77 K has two advantages: first, the Doppler width is ½ of its room temperature value; second, the rotational partition function is about 8 times smaller (for nonlinear molecules). Both of these features improve normally congested spectra.

We have taken spectra of the C-H stretching overtones of methane and of deuterated methanes in the visible. The low temperature spectrum of CH_4 shows Doppler-width features, although the spectrum is still very congested. We have also studied CD_3H at both room temperature and at 77 K. At room temperature, the rotational analysis is complicated by overlapping bands, and by incompletely resolved K-structure. We will present a rotational analysis of the low temperature spectrum of CD_3H which shows completely resolved structures.

[1]K. K. Lehmann, G. J. Scherer and W. Klemperer, J. Chem. Phys. 77, 2853 (1982).

Address of Scherer, Lehmann, and Klemperer: Department of Chemistry, Harvard University, Cambridge, Massachusetts USA

TE2. (2:15)

SUB-DOPPLER SPECTROSCOPY IN THE ν_2, ν_4, AND $2\nu_2$ BANDS OF NH_3

W. H. Weber and R. W. Terhune

Results are presented of Stark-tuned Lamb-dip measurements in the 6μm ν_4 and $2\nu_2$ bands of $^{14}NH_3$ obtained using a CO laser with an intracavity Stark cell. Some 230 lines from the isotopes $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$, and $^{13}C^{18}O$ were investigated with fields up to 30 kV/cm. Sixty-four coincidences with Stark-tuned NH_3 lines, involving several hundred Lamb dips, were assigned and analyzed. The positions of these lines relative to the CO laser lines are reported with a typical accuracy of 5-20 MHz. Model calculations of Lamb-dip spectra are also given that include power and pressure broadening and the collisionally transferred resonances. These are directly compared with observed spectra, from which we deduce values for the pressure broadening coefficients and the collisional transfer efficiency. Nuclear hyperfine structure is resolved on several lines, and from fitting one of these we obtain the value $eqQ = -4.83 \pm 0.30$ MHz for the nuclear quadrupole coupling constant in the $s2\nu_2$ (J=10, K=9) state. We see numerous examples of weak "forbidden" transitions $\Delta M_J = 0, \pm 2$, arising from the nuclear quadrupole coupling.

Double resonance experiments are also described in which a CO laser pumps a 6μm ν_4 transition while a tunable diode laser probes a 10μm ν_2 transition having a common lower level. Four different combinations of pump-probe transitions are studied. The CO laser is Lamb-dip stabilized on the pump transitions, which are tuned into coincidence with it using the intracavity Stark cell. The pump and probe beams overlap colinearly in the Stark cell. The double resonance signals appear as narrow transmission peaks on the diode laser scans. The narrowest observed widths are $\gtrsim$ 3 MHz (FWHM), a large portion of which is due to unresolved hyperfine structure. An analysis of the various broadening mechanisms indicates that the diode laser contributes less than 1 MHz to the widths. Resonances due to velocity-preserving but state-changing collisions are seen. Asymmetries between co- and counter-propagating linewidths are shown to arise from a combination of field inhomogeneity and coherent narrowing effects. The data are recorded using a computer-aided, rapid-scan, digital signal averaging technique.

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TE3. (2:32)

THE LINESHAPE OF INFRARED-MICROWAVE TWO-PHOTON TRANSITIONS: THE ν_2 BAND OF $^{15}NH_3$*

S. T. SANDHOLM, N. SHABESTARY, AND R. H. SCHWENDEMAN

A computer-coupled infrared-microwave two-photon spectrometer has been used to record the lineshapes of transitions in $^{15}NH_3$ as a function of sample pressure and microwave power. The frequency of the CO_2 laser is stabilized by monitoring the saturation dip in the fluorescence from a CO_2 sample in the laser cavity. A laboratory computer steps the microwave frequency and records the spectrum. The computer also records the frequency variation of the microwave power, which can be used to normalize the data to constant power. The lineshapes, as analyzed by means of the expression for a Voigt profile, appear to show significant changes in the center frequency and the Lorentz width as the microwave power is varied. The nature of these variations will be described and compared to predictions from the theory of two-photon absorption in a three-level system.

*This work was supported by the National Science Foundation

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TE4. (2:49)

INFRARED-MICROWAVE TWO-PHOTON SPECTRA IN THE ν_4 AND ν_6 BANDS OF CD_2CO*

K. NAKAGAWA AND R. H. SCHWENDEMAN

Infrared-microwave two-photon spectra in the 980 cm^{-1} region have been obtained for the asymmetric top molecule CD_2CO. The radiation sources are a CO_2/N_2O cw laser and backward wave oscillators operating in the 8-18 GHz region. The microwave radiation is amplified to ~20 watts by means of a traveling wave tube amplifier. The microwave frequency is stepped and the spectrum is recorded by a laboratory computer. Two-photon transitions have been observed for the ν_4 and ν_6 bands of CD_2CO. Initial assignments were based on the results of an infrared laser Stark study.[1] The ν_6 two-photon transitions have been observed in a sample cell outside the laser cavity. The ν_4 transitions are considerably weaker and were observed with an in-cavity cell.

A computer program has been implemented for theoretical calculation of the intensities of infrared-microwave two-photon transitions for an asymmetric top molecule. The calculation is complicated by the existence of many possible intermediate states and by the necessity of many summations over M components. The computational procedure will be described briefly.

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*This work was supported by the National Science Foundation.

[1] D. Coffey, Jr., C. Yamada, and E. Hirota, J. Mol. Spectrosc. 64, 98-108 (1977).

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TE5. (3:20)

DIODE LASER MEASUREMENTS OF LINE STRENGTHS AND LORENTZ HALF-WIDTHS FOR SOME LINES OF $^{14}NH_3$, $^{15}NH_3$, AND $H_2{}^{16}O$ IN THE 6.6 μm SPECTRAL REGION

V. MALATHY DEVI, B. FRIDOVICH, D.G.S. SNYDER, G.D. JONES, AND K. NARAHARI RAO.

Several line positions in the ν_4 bands of $^{14}NH_3$ have been located relative to ν_2 band lines of $H_2{}^{16}O$, and comparisons made with published values. Line strengths and Lorentz broadening coefficients have been measured for some lines in these bands. For $H_2{}^{16}O$ lines, measurements were made to determine shifts.

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TE6. (3:37)

EXPERIMENTAL AND THEORETICAL INVESTIGATION OF FOREIGN GAS BROADENING OF AMMONIA TRANSITIONS OF THE ν_2 (1 - 0) AND ν_2 (2 - 1) BANDS

G. BALDACCHINI, S. MARCHETTI [+], V. MONTELATICI, V. SORGE , G. BUFFA [=] AND O. TARRINI [=]

We have measured the broadening of several rotovibrational transitions of the ν_2 band of NH_3 caused by collisions with foreign gases as He, H_2 and N_2. As expected the values of pressure broadening are smaller than those measured previously in the case of self broadening [1]. However, a smaller broadening infers a smaller impact parameter so that the Anderson's approximation in the frame of the impact theory begings to fail. Nevertheless, we are trying to apply this theory in the case of N_2-broadening, because of the slight bigger values of the impact parameter with respect to the other gases. The results of such calculation will be presented along with a critical analysis of the experimental data.

(1) G. Baldacchini, G. Buffa, S. Marchetti, V. Montelatici and O. Tarrini: J.Chem. Phys. 76, 5271 (1982); same authors with V. Sorge: J.Chem.Phys. (1983)

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Address of Marchetti: C.N.R., Pisa, Italy
Address of Buffa and Tarrini: Istituto di Fisica, Università di Pisa, Italy.

TE7. (3:49)

MEASUREMENTS OF THE ν_3 BAND OF HCN BROADENED BY N_2 AND BY HF

M.A.H. SMITH and G. A. HARVEY

N_2-broadened halfwidths have been measured for 51 lines belonging to the ν_3 fundamental band of hydrogen cyanide ($^1H^{12}C^{14}N$). Data were obtained at room temperature (≈299K) using a Fourier transform interferometer spectrometer with a nominal resolution of 0.06 cm^{-1}. Spectra were recorded in the region from 3200 to 3400 cm^{-1}, using a 10-cm absorption cell with broadening gas pressures varying from 150 to 700 torr. The halfwidth values were obtained through a nonlinear least squares spectral fitting procedure, and are generally consistent from scan to scan. The resulting N_2-broadened halfwidths, determined for all lines with $J \leq 25$ in both the P and R branches, are smaller than CO_2-broadened halfwidths, but larger than Ar-broadened halfwidths measured for the same band[1], and also show a decrease in halfwidth for increasing J.

HF-broadened HCN halfwidths have also been measured in spectra of 3 separate 10-cm absorption cells, each filled to a total pressure of approximately 150 torr with a 50-50 mixture of HF and N_2 and containing several hundred ppm of HCN. An oscillatory dependence of the halfwidth on m , indicative of near-resonant dipole-dipole interactions between HF and HCN, has been observed and is consistent with a similar m -dependence previously measured for HCN broadened by HCℓ.[1]

[1] R. J. Thibault, A. G. Maki and E. K. Plyler, J. Opt. Soc. Am. 53, 1255 (1963).

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TE8. (4:01)

HIGH RESOLUTION LINE INTENSITY MEASUREMENTS OF THE $\nu_4 + \nu_5$ BAND OF C_2H_2

J. PODOLSKE, M. LOEWENSTEIN, AND P. VARANASI

Absolute intensity measurements have been performed at 296 K in the $\nu_4 + \nu_5$ band of $^{12}C_2H_2$ in the 7.54 μm region, using a tunable diode laser spectrometer. Experimental conditions were chosen to place the 18 R-branch lines studied in both the Doppler and Voigt profile regimes. Parameters for pressure broadening with N_2 and He were derived for several lines.

Line intensities for several of the C_2H_2 "hot band" lines in this spectral region have also been measured.

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Address of Varanasi: Laboratory for Planetary Atmospheres Research, State University of New York, Stony Brook, NY 11794.

TE9. (4:18)

NITROGEN-BROADENING OF THE INFRARED LINES OF $^{12}CH_4$, $^{13}CH_4$ AND $^{12}CH_3D$ AT LOW TEMPERATURES

P. VARANASI*, L. P. GIVER AND F. P. J. VALERO

From high-resolution (0.06 cm^{-1}) measurements of spectral transmittance at 100 K, 153 K, 200 K and 296 K in the ν_3 and ν_4 bands of $^{12}CH_4$ and $^{13}CH_4$, and in the ν_2 and ν_6 bands of $^{12}CH_3D$, we have determined accurate nitrogen-broadened line widths and their dependence upon temperature. While the simple $T^{-1.0}$ dependence prevails in all the cases, the line-widths of CH_3D are larger than those of CH_4, for the same rotational quantum-numeral designations, by nearly fifty percent. The theoretical implications will be discussed.

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* Supported by the Planetary Atmospheres Branch of the Earth and Planetary Exploration Division of NASA under Grant No. NGR 33-015-139

TE10. (4:30)

MEASUREMENT OF INTENSITIES IN THE ν_4 FUNDAMENTAL BAND OF $^{13}CH_4$ AT 153 K AND 296 K.

P. VARANASI, L. P. GIVER, and F. P. J. VALERO

Absolute intensities in the ν_4 - fundamental of $^{13}CH_4$ have been deduced from spectral transmittance measurements at 153 and 296 K, using a ^{13}C enriched (99.6 %) sample of $^{13}CH_4$ and a Fourier transform spectrometer with spectral resolution of 0.06 cm^{-1}. The line strengths are 96 - 98 percent of the corresponding values for $^{12}CH_4$. The absolute intensity of the band is 123 $cm^{-2}atm^{-1}$ at 296 K.

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TE11.

(4:47)

EXPERIMENTAL COLLISION-BROADENED LINEWIDTHS IN METHANE*

J. W. BRAULT, K. FOX, D. E. JENNINGS, J. S. MARGOLIS, AND L. R. BROWN

High-resolution spectra of vibration-rotation transitions in $3\nu_3$ of both $^{12}CH_4$ and $^{13}CH_4$ have been obtained using the Kitt Peak Fourier Transform Spectrometer and a 6 m White cell.[1] This work reports the results of measurements of self- and foreign gas-broadened linewidths in both isotopic species. The broadening gases included helium and molecular hydrogen and nitrogen. These experimental values will be compared with earlier theoretical calculations of collision-broadened linewidths.[2] Implications for atmospheric phenomena will be considered.

*This research is supported, in part, by the NASA Planetary Atmospheres Program.
[1]J. W. Brault, K. Fox, D. E. Jennings, and J. S. Margolis, Ap. J. 247, L101 (1981).
[2]G. D. T. Tejwani, P. Varanasi, and K. Fox, J. Quant. Spect. Rad. Transf. 15, 243 (1975).

Address of Brault: Kitt Peak National Observatory, Tucson, AZ 85726.
Address of Fox: University of Tennessee, Knoxville, TN 37996-1200.
Address of Jennings: Goddard Space Flight Center, Greenbelt, MD 20771.
Address of Margolis and Brown: Jet Propulsion Laboratory, Pasadena, CA 91103.

TE12.

(4:59)

THEORETICAL STUDIES OF COLLISION-BROADENED LINEWIDTHS IN METHANE*

KENNETH FOX

One of the more challenging problems in the theory of vibration-rotation transitions in gas-phase molecules is the prediction or calculation of shapes of spectral lines. An understanding of collision-broadened line shapes, widths and shifts is important in a variety of contexts, including planetary atmospheres.[1] For example, in the atmospheres of Jupiter and Earth, the systems CH_4-H_2, CH_4-He, and CH_4-N_2, respectively, are of considerable interest.[2] High resolution laboratory spectra have been measured[3] for the $v=0\rightarrow3$, $\Delta J=1$ transitions of both $^{12}CH_4$ and $^{13}CH_4$. These data will be analyzed with a view toward developing the theory of collision-broadened line widths of spherical-top molecules, including their isotopic dependence.

*This research is supported by the Planetary Atmospheres Program of the National Aeronautics and Space Administration, under Grant NAGW-125.
[1]See, e.g., J. J. Gelfand, in "Vibrational-Rotational Spectroscopy for Planetary Atmospheres" (M. J. Mumma, K. Fox, and J. Hornstein, eds.), NASA 1982.
[2]See, e.g., K. Fox in "Molecular Spectroscopy: Modern Research" (K. Narahari Rao and C. W. Mathews), Academic 1972.
[3]J. W. Brault, K. Fox, D. E. Jennings, J. S. Margolis, and L. R. Brown, preceding Abstract, this Symposium.

Address of Fox: University of Tennessee, Knoxville, TN 37996-1200.

TF1. (2:15)

HIGH SENSITIVITY HETERODYNE-POLARIZATION SPECTROSCOPY

M. RAAB AND A. WEBER

Applying heterodyne detection schemes[1] to laser polarization spectroscopy[2] increases the sensitivity (S/N ratio) considerably[3]. An acousto-optical modulator (AOM) shifts the pump frequency relative to the probe frequency by the amount of the driving frequency of the AOM thereby avoiding coherent noise due to interference of pump and probe/signal beams. At the same time the pump beam can be amplitude modulated at high frequencies (up to the MHz region) by means of the AOM thereby shifting the detection frequency towards more favorable regions of the laser noise spectrum. Interference of an optimized fraction of the probe beam with the spectroscopic signal generated through the non-linear mixing of the pump and probe beams by the medium finally amplifies the signal at a sensitivity close to the shot noise limit. Examples are given showing spectra of $^3\Pi_u \leftarrow {}^1\Sigma_g^+$ transitions of Na_2 ($\sim 10^4$ times less intense compared to the "allowed" $A\,^1\Sigma_u^+ \leftarrow X\,^1\Sigma_g^+$ transition[4]) and weak two photon absorption in a Na-heat pipe. Detection of components of the Na-D lines was accomplished in the vapor over the metal at room temperature and with $10^3 - 10^4$ atoms in the interaction volume.

[1] J. J. Snyder, R. K. Raj, D. Bloch, and M. Ducloy, Opt. Lett. 5, 163 (1980).

[2] C. Wieman and T. W. Hänsch, Phys. Rev. Lett. 36, 1170 (1976).

[3] M. D. Levenson and G. L. Eesley, Appl. Phys. 19, 1 (1979).

[4] J. B. Atkinson, J. Becker, and W. Demtröder, Chem. Phys. Lett. 87, 92, 128 (1982).

Address of Raab and Weber: Molecular Spectroscopy Division, National Bureau of Standards, Washington, D.C. 20234.

TF2. (2:32)

RADIATIVE TRANSITION PROBABILITIES AND DIPOLE MOMENTS FOR ALL VIBRATIONAL LEVELS IN THE X $^1\Sigma^+$ AND A $^1\Sigma^+$ STATES OF NaH

W. T. ZEMKE AND W. C. STWALLEY

Calculated radiative transition probabilities between all vibrational levels in the X $^1\Sigma^+$ state (v=0-21) and in the A $^1\Sigma^+$ state (v=0-29) of NaH are given. In addition, the calculated spontaneous emission lifetimes for vibrational-rotational levels (J=0,1) and the calculated dipole moments for these same levels are given.

The calculations use new hybrid potential energy curves (based on Rydberg-Klein-Rees (RKR) and *ab initio* potential curves) and new *ab initio* dipole moment functions. The RKR curve for the X state is new[1]. The RKR curve for the A state[2] and the *ab initio* curves for both states[3] are in the literature. The dipole moment functions of internuclear distance are also new[1].

[1] R. E. Olson, B. Liu, W. T. Zemke and W. C. Stwalley, to be submitted.

[2] F. B. Orth, W. C. Stwalley, S. C. Yang and Y. K. Hsieh, J. Mol. Spectrosc. 79, 314 (1980).

[3] R. E. Olson and B. Liu, J. Chem. Phys. 73, 2817 (1980).

Address of Zemke: Department of Chemistry, Wartburg College, Waverly, IA 50677.
Address of Stwalley: Iowa Laser Facility, University of Iowa, Iowa City, IA 52242.

TF3. (2:44)

CRITICAL COMPILATION OF SPECTROSCOPIC DATA FOR THE ALKALI METAL HYDRIDE MOLECULES

W. C. STWALLEY AND S. C. YANG

With support from the National Bureau of Standards, we have critically compiled spectroscopic data and related information (especially theoretical) for the diatomic alkali metal hydride (and deuteride) molecules (and ions). This includes principally the following:

1. spectroscopic constants
2. term values, dissociation energies and zero point energies
3. potential energy curves
4. laser induced fluorescence coincidences

Penultimate tabulations of these results will be presented along with major advances in information (e.g. isotopic differences in LiH). A review presenting and discussing these results is now being written and will be submitted for publication shortly after this talk. Final criticisms of and supplements to these results are solicited.

Address of Stwalley: Iowa Laser Facility and Department of Chemistry, University of Iowa, Iowa City, Iowa 52242.
Address of Yang: Department of Chemistry, University of Rhode Island, Providence, Rhode Island 02881.

TF4. (3:15)

CRITICAL COMPILATION OF SPECTROSCOPIC DATA FOR THE ALKALI METAL DIATOMIC MOLECULES

W. C. STWALLEY, W. T. ZEMKE AND R. B. BERNHEIM

With support from the National Bureau of Standards and the Joint Institute for Laboratory Astrophysics, we have critically compiled spectroscopic data and related information (especially theoretical) for the diatomic molecules (including ions) containing Li, Na, K, Rb and Cs only. This includes principally the following:

1. spectroscopic constants
2. term values, dissociation energies and zero point energies
3. potential energy curves
4. laser induced fluorescence coincidences
5. optically pumped laser transitions

Penultimate tabulations of these results will be presented along with examples of major advances in information (e.g. much more accurate dissociation energies). A review presenting and discussing these results is now being written and will be submitted for publication shortly after this talk. Final criticisms of and supplements to these results are solicited.

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Address of Zemke. Department of Chemistry, Wartburg College, Waverly, Iowa 50677.
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TF5. (3:32)

NEW OPTICALLY-PUMPED ALKALI METAL DIATOMIC LASERS

J. T. BAHNS, A. R. RAJAEI-RIZI, K. K. VERMA, F. B. ORTH AND W. C. STWALLEY

We have obtained many new optically-pumped laser (OPL) lines when dimers of sodium and lithium are pumped with an argon ion or krypton ion laser. These large frame lasers (operated on a single longitudinal mode) are used to excite $B^1\Pi_u \rightarrow X^1\Sigma_g^+$ (for Na_2 and Li_2) and $A^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ (for Na_2) multiline laser oscillation of these dimers in a ring cavity. Analysis of the associated fluorescence spectra results in the assignment of most OPL lines.

In addition to the (predominantly) bound-bound OPL transitions (including lower laser levels up to dissociation), in the case of pumping sodium dimers (with the 568.2 nm output of a krypton ion laser) stimulated bound-free emissions have been observed for the first time between two strongly bound molecular states ($A^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ continuum) at ~805 and 817.5 nm.

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TF6. CANCELLED

Laser Excited Fluorescence of Na_2: Intensities in the A-X and B-X Transitions

K.S. Chandrasekhar, T.K. Balasubramanian, K. Raghuveer and N.A. Narasimham

Fluorescence was excited in the A-X and B-X systems of Na_2 using the 6328 A line of a home built He-Ne laser (30 mW) and 4880 A and 5145 A lines of a Commercial Ar^+ laser (800 mW), operating in multimode. Sodium dimers were produced in a heat pipe oven fabricated in our laboratory. The fluorescence was recorded on a SPEX Ramalog double monochromator employing photon-counting detection. A standard lamp (No.127C, NPL, Teddington) was used for the calibration of the spectrometer and the intensities of the lines of the fluorescence series were determined quantitatively.

The FCF and R-Centroid for each transition was computed by standard procedure and the variation of the electronic transition moment with R-Centroid for both the systems has been studied. In the course of these investigations two additional fluorescence series - (v'-7, v") Q(25) and (v'-7, v") R(29), P(31) in the B-X system, for 4880 A excitation have been identified. The positions of all the lines could be reproduced satisfactorily by the constants provided by Kusch and Hessel (1).

(1) P. Kusch and M.M. Hessel : J. Chem. Phys., 68, 2591 (1978)

Address: Spectroscopy Division, Bhabha Atomic Research Centre, Trombay, Bombay-400 085, India

TF7. (3:49)

METHOD FOR CALCULATING HIGH-ORDER RKR POTENTIAL

R. J. LE ROY, AND P. PAJUNEN

The familiar quadrature form of the RKR inversion procedure for determining diatomic molecule potential energy curves from spectroscopic data is generalized using an iterative procedure which takes account of higher-order terms in the phase-integral (or JWKB) approximation on which this method is based. For little extra computational cost, the new method yields potential energy curves which are much more accurate than those obtained from the familiar first-order procedure. The method will be described and tested on the ground state of Li_2.

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TF8. (4:06)

OPTICALLY DETECTED MAGNETIC RESONANCE OF SEVERAL CARBONYL COMPOUNDS ADSORBED ON ALUMINA

A. M. NISHIMURA

The results of some preliminary study of carbonyl containing compounds adsorbed on alumina is reported. Initially, adsorption isotherms of these compounds from solution were characterized. The concentration of the solution was adjusted for maximum coverage on the alumina. The adsorbed molecules were then optically pumped and surface emission was monitored. Results of the optically detected magnetic resonance studies indicate that information regarding possible orientation might be obtained by this technique.

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TF9. (4:18)

INFRA RED OPTICAL DOUBLE RESONANCE SPECTROSCOPY OF ND_2*

R. E. MUENCHAUSEN AND G. W. HILLS

This preliminary work demonstrates the utility of the infra red optical double resonance technique (IODR) in the investigation of the optical absorption spectrum of ND_2 in the region 5400-6250 Å.

A CO_2 gas infra red laser pumped ortho rotational transitions within $\tilde{X}\ ^2B_1$, $5_{05}-5_{14}$, F_1-F_1 and $2_{12}-2_{21}$, F_2-F_2 in the ν_2 band using the $^{12}C^{18}O_2$ P(10) line at 1076.578 cm^{-1} and $^{12}C^{16}O_2$ R(26) line at 1082.302 cm^{-1} respectively. A counter-propagating CW dye laser was tuned through bands of the $\tilde{A}\ ^2A_1 \leftarrow \tilde{X}\ ^2B_1$, visible system and the IODR signals were detected as changes in the fluoresence at the IR chopping frequency.

IODR signals corresponding to decreases in fluorescence were observed for optical transitions from both directly pumped (3-level) and collisionally linked (4-level) ortho rotational levels in $\tilde{X}$ (0,0,0). Increased fluoresence IODR signals were also observed in both 3- and 4- level schemes for optical transitions involving ortho rotational levels in $\tilde{X}$ (0,1,0).

In addition to simplification of the optical spectrum, which facilitates assignments, observation of IODR signals was used to investigate a perturbation involving the $1_{11}\ \Pi(0,12,0)$ level by accurately locating the perturbing level. This study illustrates how the specificity of the IODR technique, in selecting a particular rotational level within a dense manifold of levels, can be utilized.

*Research supported by the National Science Foundation under grant CHE-8111131

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TF10. (4:35)

OPTOGALVANIC SPECTROSCOPY IN LOW PRESSURE DISCHARGES WITH COLOR-CENTER AND DYE LASERS

R. D. MAY, Z. ZHU, AND G. W. HILLS

Rydberg-Rydberg transitions in hollow cathode discharges through pure Xenon and Krypton gases have been observed using an F-center laser. Signals of both positive and negative polarities are seen and can be explained in terms of laser induced effects on the steady state ionization processes occurring in the discharge. Optogalvanic signals are also observed in the 3650-3780 cm^{-1} region in a low current discharge in pure CO_2 using the F-center laser. Work is currently under way to identify this spectrum.

Transitions in the visible region have been observed in an rf dischage in CH_2CO but are apparently not due to CH_2. Current investigations are directed at attempts to detect other free radicals in rf or dc discharges using tunable IR and dy lasers and optogalvanic detection.

This research was supported by the National Science Foundation under grant CHE-8111131.

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TF11. (4:47)

Laser Induced Fluorescence Spectra of Free-Jet Cooled Organic Free Radicals - Vinoxy, Cyclopentadienyl, and Benzyl

M. C. Heaven, Terry A. Miller and L. DiMauro.

The organic free radicals, vinoxy, cyclopentadienyl, and benzyl, have been produced *in situ* in a free jet expansion by excimer laser photolysis of suitable precursors. Rotationally resolved, laser induced fluorescence spectra, obtained downstream of the photolysis, show the gaseous radials are cold (∿ 10°K). Details of the rotational analyses will be presented.

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TF12. (4:59)

DIRECT OBSERVATION OF $^3\Pi_g$ STATES OF THE Na_2 MOLECULE BY OPTICAL-OPTICAL DOUBLE RESONANCE

LI LI and ROBERT W. FIELD

Six Na_2 vibrational levels of $^3\Pi_{0g}$ symmetry have been observed near 34000 cm^{-1} by Optical-Optical Double Resonance (OODR) fluorescence excitation spectroscopy. Na_2 molecules were excited from the $X^1\Sigma_g^+$ state, using a single-mode cw dye laser, to singlet-triplet mixed J=13,14, or 15 levels of the $b^3\Pi_{0u}v=24\sim A^1\Sigma_u^+$ v=22 perturbation complex.[1] OODR transitions into the $^3\Pi_{0g}$ levels were detected by monitoring $^3\Pi_{0g}\rightarrow a^3\Sigma_u^+$ fluorescence near 430 nm as the wavelength of a second cw dye laser was scanned.

The levels observed

	T_{vo}	B_v
v*	33761.86 cm^{-1}	0.0601 cm^{-1}
v* + 1n	33868.19	0.0583
v* + 2n	33971.95	0.0567
v* + 3n	34072.88	0.0559
v* + 4n	34171.04	0.0549
(n = 1 or 2)		
v**	34134.16	0.0794

belong to two $^3\Pi_{0g}$ states. The triplet character of these states was evident from the greater intensity of OODR excitation out of levels of predominant $b^3\Pi_u$ (extra lines) rather than $A^1\Sigma_u^+$ (main lines) character. The $^3\Pi_0$ assignment was based on the absence of Q branch lines.

[1] J.B. Atkinson *et al.*, Chem. Phys. Lett. 87, 92 (1982), (tentative v_Π assignment).

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TG1. (2:15)

SOME MICROWAVE AND INFRARED OBSERVATIONS ON THE METHANOL C-O STRETCH STATE

R.M. LEES*, P. MCGHEE, R.R.J. GOULDING AND I. MUKHOPADHYAY

Several microwave transitions of the $J = 2 \leftarrow 1$ $v_t = 0$ a-type multiplet in the excited C-O stretch state have been observed for CH_3OH. Also, a number of the $k = 1$ asymmetry doublets of the A torsional species in the $v_t = 1$ torsional state have been identified in the P and R branches of the diode laser spectra of the C-O stretch band[1] and in Fourier transform spectra of this band obtained from the Herzberg Institute of Astrophysics. The measured frequencies will be discussed in terms of the molecular constants, in particular the set of constants plus empirical corrections proposed by Henningsen.[2] In addition, comments will be made on the IR-IR 3-level double resonance observed with the 9P(34)CO_2 laser line by Drs. R.R. Dasari and M. Feld at the Regional Laser Center, M.I.T., which confirms Henningsen's $(n\tau K) = (125)$ assignment for the pumped CH_3OH transition, and on Henningsen's suggested identification of the X state with the in-plane CH_3 rock.

[1] J.P. Sattler, W.A. Riessler and T.L. Worchesky, Infrared Phys. 19, 217-224 (1979).

[2] J.O. Henningsen, J. Mol. Spectrosc. 85, 282-300 (1981).

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TG2. (2:32)

FOURIER TRANSFORM INFRARED SPECTRUM OF METHYLAMINE FROM 50 - 125 CM^{-1}

M.S. MALGHANI, R.M. LEES AND R.T. ADSETT

The far infrared spectrum of CH_3NH_2 has been obtained in the 50 - 125 cm^{-1} region at 0.02 cm^{-1} and 0.005 cm^{-1} resolution using Dr. J.W.C. Johns' Bomem Fourier transform spectrometer at the Herzberg Institute in Ottawa. Of the numerous well-defined R-branches present in the spectrum, we have so far identified most of the $(J+1,k+1) \leftarrow (J,k)$ c-type series with $|k|$ values from 7 to 14 for the A^a and E^a torsion-inversion symmetries. The corresponding Q branches are weak, and few have been observed directly in the spectrum. By extrapolation of the R branches back to the origin, we have obtained Q-branch origin frequencies with estimated 0.03 cm^{-1} accuracy to fit to the customary semi-empirical model containing various distortional constants. The results of our filtered least-squares fit to the extrapolated infrared and available microwave data will be reported.

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TG3. (2:45)

MICROWAVE SPECTRA OF PERFLUOROETHYLENE OXIDE

J. AGOPOVICH, C. GILLIES, AND T. RAW

The microwave spectrum of oxygen-18 enriched perfluoroethylene oxide was investigated in the region of 26.5 to 40 GHz. The groundstate rotational constants (MHz) are A = 4234.51, B = 2518.13 and C = 1949.79. Vibrationally excited states of the normal isotope and the carbon 13 species in natural abundance are currently being studied. These data will be related to infrared assignments[1] and the isotopic work will be used to discuss the molecular structure.

[1] N.C. Craig, Spectrochimica Acta, 28A, 1195 (1972).

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TG4. (3:31)

MICROWAVE SPECTRA OF TRANS-1,2-DIFLUOROETHYLENE OXIDE

G. LABRECQUE, J. AGOPOVICH, AND C. GILLIES

The microwave spectra of trans-1,2-difluoroethylene oxide was investigated in the region of 26.5 to 40 GHz. A fit of the near-prolate μ_b-type spectrum gave the following rotational constants (MHz) for the ground state normal isotope: A = 14731.47, B = 3582.85 and C = 3222.44. The electric dipole moment was measured to be $\mu_b = \mu_T = 1.11$D. The dideutero species, CDFCDFO, and the oxygen-18 species, $CHFCHF^{18}O$, have been assigned and presently work is in progress on the carbon-13 isotopic assignment. The isotopic data will be used to discuss the molecular structure.

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TG5. (3:35)

MICROWAVE SPECTRUM OF CH_2DSH

CHUN FU SU AND C. RICHARD QUADE

Last year at this meeting we reported our preliminary results for the torsional-rotational spectra of CH_2DSH and CHD_2SH. At the current meeting we will report additional data for CH_2DSH and the results of our analysis. The Hamiltonian for the analysis of the spectroscopic data for the three substates of the torsional ground state has the form

$$H_\sigma = A_\sigma P_z^2 + B_\sigma P_y^2 + C_\sigma P_x^2 + \beta_\sigma J(J+1)K^2 + \gamma_\sigma J^2(J+1)^2 + \mathcal{E}_\sigma$$

$$H_{e_1,o_1} = Q'P_z + D'(P_xP_y+P_yP_x) + E'(P_xP_z+P_zP_x) \quad .$$

The spectroscopic coefficients as determined by a least squares fit are

$A_{e_o} = 86040$ MHz	$A_{e_1} = 86481$ MHz	$A_{o_1} = 85079$ MHz
$B_{e_o} = 12125$	$B_{e_1} = 11835$	$B_{o_1} = 11849$
$C_{e_o} = 11430$	$C_{e_1} = 11638$	$C_{o_1} = 11624$
$\beta_{e_o} = 0.23$	$\beta_{e_1} = -3.99$	$\beta_{o_1} = 3.50$
$\gamma_{e_o} = 0.039$	$\gamma_{e_1} = 0.176$	$\gamma_{o_1} = -0.03$

$\Delta = 12830$MHz $\qquad V_3 = 449\text{cm}^{-1}$

$Q' = 4400 \qquad V_1 = 10$

$D' = 40$

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TG6. (3:52)

HIGH RESOLUTION SPECTROSCOPY OF VIBRATIONALLY EXCITED FLUOROFORM-D BY HETERODYNE FREQUENCY MEASUREMENT OF SMMW LASER EMISSION

M. S. TOBIN, R. P. LEAVITT, T. W. DALEY, AND W. G. TRUEHEART, JR.

Submillimeter wave laser action has been previously reported[1] in deuterated fluoroform (CDF_3) which is optically pumped by a CO_2 laser. In this paper, accurate heterodyne measurements are reported for the frequencies of 21 of these laser emissions. Nineteen of these lines can be assigned to the ν_5 degenerate vibrational state. The data were fit with a theoretical expression for the frequencies containing terms up to sixth order in J and K and also containing all important ℓ-doubling effects. The quality of the fit was excellent, yielding accurate values for many of the molecular constants of the ν_5 state.

[1] M. S. Tobin and R. D. Felock, Opt. Lett. 5, 430 (1980).

Address of Tobin, Leavitt, Daley, and Trueheart: U.S. Army Electronics Research and Development Command, Harry Diamond Laboratories, 2800 Powder Mill Road, Adelphi, MD 20783

TG7. (4:04)

ROTATIONAL SPECTRA OF 16-17-16 AND 17-16-16 O_3

E. A. Cohen and H. M. Pickett

The rotational spectral and hyperfine structure of 16-17-16 and 17-16-16 O_3 have been observed and analysed. The spin-rotation tensors of both molecules are characterized by large values of M_{aa}. These are 172(14) kHz and 257(9) kHz for the 16-17-16 and 17-16-16 species, respectively. The spin-rotation and quadrupole tensors will be discussed in terms of a simple molecular model.

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TG8. (4:16)

ROTATIONAL SPECTRA OF VIBRATIONALLY EXCITED OZONE

H. M. Pickett and E. A. Cohen

Many new lines of vibrationally excited ozone have been found in the spectral region from 8 to 300 GHz. Lines for the (010) and (020) states are fit to a Watson S-type Hamiltonian. Lines for the (100) and (001) are fit using an interacting states model. Work is in progress to make a combined fit of microwave and infrared lines for (100) and (001) to an accuracy consistent with both data sets.

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TG9. (4:28)

MICROWAVE SPECTRA AND STRUCTURE OF METHYLGERMYL CYANIDE

A. B. MOHAMAD AND J. R. DURIG

The microwave spectra of $CH_3{}^{70}GeH_2CN$, $CH_3{}^{72}GeH_2CN$, $CH_3{}^{74}GeH_2CN$, $CH_3{}^{70}GeD_2CN$, $CH_3{}^{72}GeD_2CN$ and $CH_3{}^{74}GeD_2CN$ have been recorded in the K-band region. Only a-type transitions have been observed and R-branch assignments have been made for the ground vibrational state. The ν structural parameters have been obtained using the diagnostic least-squares adjustment to fit the rotational constants. These results will be compared to the corresponding quantities in some similar molecules.

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AD-A133 957 SYMPOSIUM ON MOLECULAR SPECTROSCOPY (38TH) HELD AT OHIO STATE UNIVERSITY COLUMBUS OHIO ON JUNE 13-17 1983(U) OHIO STATE UNIV COLUMBUS 1983 2/2

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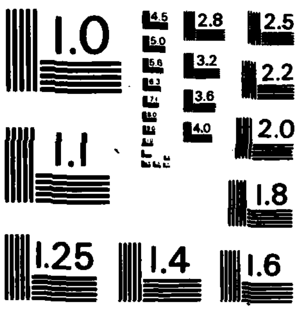

TG10. (4:40)

OBSERVATION OF VISIBLE ABSORPTION IN THE FOURTH OVERTONE OF THE OH STRETCH IN GASEOUS CH_3OH

G.O. Brink

Several absorption bands corresponding to the fourth overtone of the OH stretch have been observed in the visible portion of the spectrum in gaseous methanol. The technique used is that of dye laser intracavity absorption in which an absorption cell containing the sample is placed inside the cavity of a tunable dye laser. The laser is repetitively scanned in wavelength, and its output observed by means of a 3 meter spectrograph and an optical multichannel analyzer.

Several bands are observed in the vicinity of 600 nm. At the spectral resolution used no structure is observed in these bands, and they appear to be about 0.15 nm wide. They are anomalously strong which is probably due to the clustering of many unresolved rotational levels. Their strength is comparable with water vapor absorption in this spectral region. Attempts are being made to determine their strength absolutely by comparison with absorption in an atomic beam of sodium.

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TH1. (2:15)

A KINETIC STUDY OF THE THERMAL DECOMPOSITION OF 2,2,4,4-TETRAMETHYLCYCLOBUTANEDIONE USING TIME-RESOLVED FTIR

DAVID LATHAM, J. BAIARDO, R. MUKHERJEE, S. PASZYC, AND M. VALA

Spectroscopic methods have been used for years to follow chemical processes. We have used FTIR spectroscopy to follow the thermal decomposition of 2,2,4,4-tetramethylcyclobutanedione (TMCBD) into one of its products, dimethylketene (DMK). This process is too fast to be followed accurately by standard IR spectroscopic methods. Using the time-resolved Fourier transform technique, many spectra can be collected in a very short period of time. This allows us to calculate the standard kinetics parameters by following the integrated peak areas of the TMCBD and DMK as a function of time.

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TH2. (2:32)

FOURIER TRANSFORM INFRARED SPECTRA OF $2NH_3 \cdot D_2O$ and $2ND_3 \cdot H_2O$, at 15°K

John E. Bertie and J.P. Devlin

$2NH_3 \cdot D_2O$ and $2ND_3 \cdot H_2O$ have been made by mixing the protonated and deuterated species as they condense onto a cesium iodide plate at ~80°K, and crystallizing the consequent glass at 120°K. ND_3 has been incorporated at low concentrations into $2NH_3 \cdot D_2O$ and $2NH_3 \cdot H_2O$, as has NH_3 into $2ND_3 \cdot D_2O$ and D_2O into $2NH_3 \cdot H_2O$. The mid-infrared spectra of these samples at 15°K and temperatures up to 80°K provide information about the low-temperature phase and the lambda, specific-heat, transitions at 51.6 and 53.3°K.

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TH3. (2:45)

VIBRATIONAL SPECTRA OF SOLID $CF_3C\ell$, $CF_2C\ell_2$ AND $CFC\ell_3$*

D. D. FONTAINE AND G. E. LEROI

In order to derive information pertaining to the crystal symmetries of the chlorofluoromethanes, for which diffraction measurements have not been reported, we have obtained far infrared and Raman spectra of solid $CF_3C\ell$, $CF_2C\ell_2$ and $CFC\ell_3$. Spectra have been observed between 13-130°K; no evidence of phase changes for any of these halomethanes over this temperature range is noted.

The lattice spectra are consistent with crystal structures which vary smoothly between the low-temperature forms of CF_4 ($P2_1/c, Z=4$)[1] and $CC\ell_4$ ($C2/c, Z=32$).[2] Mutual exclusion between infrared and Raman activity is found, as expected for centric unit cells. The symmetry-forbidden a_2 fundamental (ν_5) of $CF_2C\ell_2$ is observed in the infrared spectrum of the crystalline solid, which indicates a site symmetry lower than the C_{2v} molecular symmetry. Three infrared peaks are observed for the $\nu_4(a_1)$ mode; they are interpreted in terms of the $C\ell$ isotopes in natural abundance. Implications of the spectroscopic observations on the crystal symmetries of solid $CF_3C\ell$, $CF_2C\ell_2$ and $CFC\ell_3$ will be discussed.

Molecular packing considerations[3] have also been applied to these crystals. The resultant molecular geometries have been employed in lattice dynamics calculations for the chlorofluoromethanes, which will also be described.

*Research supported in part by the U. S. National Science Foundation.

[1] R. Powers and R. Rudman, J. Chem. Phys. 72, 1629 (1980).

[2] S. Cohen, R. Powers and R. Rudman, Acta Cryst. B35, 1670 (1979).

[3] D. E. Williams, PCK5/PCK6, QCPE 12, 373 (1979).

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TH4. (3:00)

FAR INFRARED SPECTRUM OF THE LOW-TEMPERATURE PHASE OF SOLID $CC\ell_4$*

D. D. FONTAINE AND G. E. LEROI

The structure of the low-temperature form (phase II) of solid $CC\ell_4$ has been determined from X-ray diffraction[1] to be monoclinic, space group C2/c, with 32 molecules per unit cell. A "reduced" cell with Z=4 has been invoked to interpret previous far infrared spectra,[2] and the reported Raman spectra are not inconsistent with the simpler cell.[3] We have obtained (interferometric) far infrared spectra of solid (II) $CC\ell_4$ in the 13-80°K range which show at least 13 peaks at the lowest temperature. These are the first spectroscopic results which are consistent only with the established crystal structure.

Atom-atom intermolecular potentials of the Lennard-Jones form have been proposed for the liquid and solid cubic (Ia) phases of $CC\ell_4$.[4] The applicability of these potentials for lattice dynamics calculations of the low-temperature solid phase (II) of $CC\ell_4$ will be described.

[1] S. Cohen, R. Powers and R. Rudman, Acta Cryst. B35, 1670 (1979).

[2] A. Anderson, B. H. Torrie and W. S. Tse, Chem. Phys. Letters 61, 119 (1979).

[3] R. J. H. Clark and B. K Hunter, J. Chem. Soc. (A) 1971, 2999 (1971); H. F. Shurvell, Spectrochim. Acta 27A, 2375 (1972).

[4] R. Righini and M. L. Klein, Chem. Phys. Letters 87, 604 (1982); I. R. MacDonald, D. G. Bounds and M. L. Klein, Mol. Phys. 45, 521 (1982).

*Research supported in part by the U.S. National Science Foundation.

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TH'1. (3:30)

ESR OF Cr METAL MOLECULES AT 4°K

R.J. VAN ZEE, C.A. BAUMANN, AND W. WELTNER, JR.

Natural Cr (I = 0) and ^{53}Cr (I = 3/2) (enriched to 96.9%) metals were vaporized and trapped in neon and argon matrices at 4°K. X-band ESR spectra contained at least 15 fine structure lines belonging to two molecules, besides those due to Cr atoms. Hyperfine splitting patterns showed that Cr_2 was not observed, supporting the assignment of its ground state as $^1\Sigma$.

Tentative analysis of the spectra indicates that both molecules are of high spin with the unpaired electrons in each interacting almost entirely with one Cr nucleus. Eight lines can be definitely assigned to one axial molecule (perhaps Cr_4 with C_{3v} symmetry) and can be fit to within 3G with the following parameters: S = 3, $g_\perp$ = 1.9970(2), $g_\parallel$ = 1.9996(5), |D| = 0.1103(3) cm^{-1}, $|A_\perp$ (unique $^{53}Cr)|$ = 71.6(14) MHz. The remaining lines appear to belong to an axial molecule with S = 4 or 5, which could be a slightly bent Cr_3 with C_{2v} symmetry, in essential agreement with the Raman work of DiLella, et al.[1] Only the spectrum of this molecule appears in argon matrices.

[1] D.P. DiLella, W. Limm, R.H. Lipson, M. Moskovits, and K.V. Taylor, J. Chem. Phys., 77, 5263 (1982).

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TH'2. (3:47)

ESR OF PSEUDOROTATING $^6Li_3$ AND $^7Li_3$

D. A. GARLAND AND D. M. LINDSAY

ESR spectra assigned to pseudorotating $^6Li_3$ and $^7Li_3$ molecules have been produced by arc lamp photolysis of argon matrices doped with isotopically enriched ^6Li or ^7Li. The spectrum of $^6Li_3$ consists of 7 equally spaced first derivative transitions with relative intensities (1.1:3.3:6.2:7.0:5.7:3.0:1.1) in good agreement with the expected values for 3 equivalent I = 1 nuclei. The measured hf constant and g value are <a> = 12.21(1) G and g_0 = 2.00282(1). The absence of a "stationary" trimer spectrum suggests that the ground vibronic state of Li_3 is non-localized as predicted by ab initio calculations.[1] The total isotropic spin population of the trimer ($\Sigma\rho$ = 0.68) suggests that the unpaired electron wave function has an approximately 30% p-character. A comparison of the orbital composition of M, M_2, M_3, M_∞ (M = Li, Na, K) shows (i) a diminishing s-character with increasing cluster size, (ii) a remarkable similarity between Na and K cluster for all sizes, and (iii) a markedly smaller s-character for Li clusters.

[1] W.H. Gerber and E. Schumacher, J. Chem. Phys. 69, 1697 (1978).

Address of Garland and Lindsay: Department of Chemistry, City University of New York, The City College, Convent Ave. at 138th St., N.Y., N.Y. 10031.

TH'3. (4:04)

TWO-PHOTON SPECTROSCOPY OF Cu^+ IN ALKALI HALIDE HOST CRYSTALS

Stephen A. Payne, Andrea Goldberg and Donald S. McClure

The 3d→4s transitions of Cu^+ become, in cubic host crystals, $^1A_{1g} \rightarrow {}^1E_g$, $^1T_{2g}$ as well as several singlet-triplet transition. Two-photon spectroscopy is capable of clearly separating the overlapping ^1E_g and $^1T_{2g}$ spectra by virtue of the polarization selection rules. In cases where the Cu^+ ion lies off-center in its halide octahedron ($KCl:Cu^+$), the two-photon spectra show bands with mixed symmetries. In a series of alkali chlorides, the crystal field and Jahn-Teller parameters have been determined and compared. In addition, the average extent to which the Cu^+ departs from the center can be inferred from the spectra.

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TH'4. (4:21)

EXCITED STATE DYNAMICS OF Cu^+ IN NaF HOST CRYSTAL

Andrea Goldberg, Stephen A. Payne and Donald S. McClure

The one- and two-photon spectra of $NaF:Cu^+$ showed a zero phonon line and a progression of the t_{1u} mode (Cu^+ moving off-center) in the $^1A_{1g} \rightarrow {}^1E_g$, $^1T_{2g}$ transitions at 2°K. The spectra have been fitted with a 3-dimensional mixed quartic-harmonic potential including a crystal field term. The increasing widths of successive members of the progression are related to the increasing density of states of the NaF lattice. Coupling of the t_{1u} mode to the Jahn-Teller potential in the ^1E_g state has clearly observable effects. Other aspects of this unusual example will be discussed.

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TH'5. (4:38)

ZEEMAN SPLITTING OF THE PHOSPHORESCENCE OF PALLADIUM-PHTHALOCYANINE IN A SHPOLSKI'I MATRIX

W.-H. Chen, K.E. Rieckhoff, and E.-V. Voigt

The Zeeman splitting in the lowest phosphorescence state of palladium-phthalocyanine in a Shpolski'i matrix of mixed α-chloronaphthalene and n-octane at 20 K is reported. The evidence shows that this state is indeed a triplet and that in zero magnetic field the unperturbed component is about 0.7 cm^{-1} higher than the field sensitive degenerate pair. A g-factor of about 2.4 is calculated from the splitting which indicates that the states are not pure spin states.

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TH'6. (4:50)

THE EFFECT OF PRESSURE ON MOLECULAR RYDBERG TRANSITIONS

J.L. ADOLPH, D.L. BESTWICK AND J.D. SCOTT

The effect of certain external perturbations on the absorption spectrum of a molecular sample can be measured as

$$A^P(\tilde{\nu}) = \tilde{\nu} \sum_{j=o} Cj\, d^j[A^\circ(\tilde{\nu})/\tilde{\nu}]/d\tilde{\nu}^j$$

where $A^P(\tilde{\nu})$ and $A^\circ(\tilde{\nu})$ are the absorption curves with and without perturbation and the Cj's are coefficients dependent on the nature and intensity of the perturbation. If these coefficients can be expressed in context of molecular-structure parameters then direct contact between experiment and molecular properties may be made.

We shall discuss a van der Waals interaction model we are developing to account for the effect a high-pressure non-absorbing gas has on the absorption bands associated with Rydberg transitions of various molecular species. The specific system we use as an example is the first s-Rydberg transitions of methyliodide (CH_3I) in the presence of SF_6.

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WE1. (1:30)

HUND'S COUPLING CASES AND TETRAHEDRAL SPLITTINGS IN ROTATIONAL LEVELS OF ELECTRONIC $^2F_2$ STATES IN ND_4

G. HERZBERG AND J. T. HOUGEN

The Schüler band of the Rydberg radical ND_4 lying near 14 800 cm^{-1} is presumed to arise from the $(5s)^2A_1$ - $(3p)^2F_2$ transition, where identification of the lower state rests in part upon the isotope-independent 6 cm^{-1} spin splitting observed between a pair of heads in emission spectra photographed for both NH_4 (diffuse) and ND_4 (sharper).

Any attempt at a detailed rotational analysis of this spectrum requires a knowledge of rotational levels in a tetrahedral molecule exhibiting both spin-orbit interaction and tetrahedral splittings. Such rotational levels can be determined relatively easily by combining with suitable modifications the usual CH_4 vibration-rotation Hamiltonian and the usual NO spin-orbit and spin-rotation Hamiltonian. The principal qualitative effects of these interactions on the rotational levels will be described and some examples of stick spectra calculated from a computer program with appropriate matrix elements in a D_{2d} basis set will be shown.

Unfortunately, even with this program, the Schüler band has to date eluded unambiguous assignment, and the extreme overlapping of lines in the region of the two heads may ultimately preclude more than a qualitative theoretical fit of the observed data.

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Address of Hougen: Molecular Spectroscopy Division, National Bureau of Standards, Washington, DC 20234, USA.

WE2. (1:47)

LOCAL MODE BEHAVIOR IN THE STRETCHING OVERTONES OF GERMANE

A. G. ROBIETTE, A. S. PINE, AND S. J. DAUNT

The Ge-H stretching overtone band near 4155 cm^{-1} has been recorded with Doppler-limited resolution, for both natural GeH_4 and enriched $^{74}GeH_4$, using a difference-frequency spectrometer. The structure has been analyzed in terms of a closely-coupled $A_1 + F_2$ pair of bands for each isotopic species. The vibrational modes are best described not as $2\nu_1$, $\nu_1 + \nu_3$ or $2\nu_3$ levels but rather as a (2000) local mode cluster. The rotational coupling between the A_1 and F_2 substates leads to a complex spectrum, which has been successfully modeled and fitted to around J=10 to 12. Over 1650 assignments for the five isotopic species have been fitted with a standard deviation of around $3*10^{-4}$ cm^{-1}.

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Address of Pine: Molecular Spectroscopy Division, National Bureau of Standards, Washington, D.C. 20234.
Address of Daunt: Department of Chemistry, Concordia University, Montreal, Quebec, Canada H3G 1M8 and Molecular Spectroscopy Laboratory, Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996-1200.

WE3. (2:04)

COMBINATIONS AND OVERTONES OF CF_4

A. S. PINE AND A. G. ROBIETTE

The $2\nu_1 + \nu_4$, $2\nu_1 + \nu_3$ and $2\nu_3$ bands of CF_4 have been recorded at T=77K with Doppler-limited resolution using a tunable difference-frequency laser. The low temperature increases the resolution by reducing the Doppler width and greatly simplifies the spectra by eliminating hot bands and suppressing the population for J<40. The $2\nu_1 + \nu_4$ band is relatively isolated and unperturbed, and its previously unresolved Q branch has been analyzed in the diagonal F4 coefficient approximation yielding m=2445.59644(2) cm^{-1}, v=-6.54004(22)*10^{-4} cm^{-1} and g=-2.48897(43)*10^{-5} cm^{-1} with a fit good to 1.1*10^{-4} cm^{-1} rms. The $2\nu_1 + \nu_3$ band is strongly affected by Fermi resonance with $2\nu_1 + 2\nu_4$, and this resonance is presently being analyzed. The $2\nu_3$ spectrum shows a dominant F_2 component, but Coriolis coupling to the E component is also important in determining the detailed rotational structure. One striking feature of $2\nu_3$ is a high J subband-head within the Q° branch which had been mistakenly identified as the band center in prior lower resolution studies.

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WE4. (2:21)

LINE STRENGTHS OF THE ν_2 AND ν_4 BANDS OF $^{12}CH_4$

M.LOETE and J.C.HILICO

Using a tensorial formalism in the Td group, we have determined all the vibration-rotation operators of the dipole moment of XY_4 molecules, up to any order of approximation [1]. This general formalism is available for any transition between vibrational sublevels of whatever symmetry. It can be used for the analysis of isolated bands and for the analysis of interacting bands as well. The theory will be applied to the analysis of rovibrational line strengths of the two bands ν_2 and ν_4 of $^{12}CH_4$ alone and as a polyad, on the basis of a second order expansion of the dipole moment.

Five operators are needed to analyse the strengths of the isolated ν_4 band. It will be shown that the empirical Hermann-Wallis polynomial is not adapted to this problem, especially in the case of the "forbidden" lines. The I.R "forbidden" ν_2 band has been analysed as an isolated band with two operators.

As pointed out by many authors, the best model for these two interacting bands is the diad scheme. On this basis, we have also analysed the line strengths with the adapted second order expansion of the dipole moment. The physical meaning of the obtained parameters, which depends on the used scheme, will be also discussed.

---

[1] M.LOETE, Can. J. Phys., in press.

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WE5. (2:33)

THEORETICAL AND EXPERIMENTAL STUDY OF LINE STRENGTHS IN THE $\nu_3 - \nu_4$ HOT BAND OF METHANE

J.C.HILICO, M.LOETE and L.R.BROWN

The $\nu_3 - \nu_4$ hot band of methane is one of the main absorbing features in the 5-6 µm region which corresponds also to the ν_2 R-branch. Absolute intensities of rotational lines of this band have been measured and then analysed on the basis of the general expansion of the dipole moment operator in XY_4 molecules [1], using both spherical and tetrahedral formalism.

It will be shown that the first term (in $q_3\ q_4$) in the transformed dipole moment operator is not sufficient and that the three first order intensity parameters are necessary to reproduce the observed strengths. Using the spherical scheme, the usual assumption that (J,R,C,n) are "good quantum numbers" in the two involved vibrational levels ($v_3 = 1$) and ($v_4 = 1$) [2] is also found to be not sufficient.

[1] M.LOETE, J. Can. Phys., in press.
[2] F.PASCAUD and M.DANG-NHU, J. Mol. Spectrosc. 69, 141-158 (1978)

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WE6. (2:45)

THE ANHARMONIC CONSTANTS AND FORCE FIELD OF SF_6

B. J. KROHN, R. S. McDOWELL, J. L. LYMAN, AND J. OVEREND

A large collection of combination and difference bands of SF_6 has been analyzed to determine new values for several anharmonic consants of SF_6. These constants are then used to predict positions of hot bands and to synthesize the absorption contours in the ν_3 and ν_4 regions. A Morse-Urey-Bradley force-field model is constructed which reproduces the values of eight observed stretching anharmonicities with an r.m.s. deviation of less than 20%.

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Address of Overend: Department of Chemistry, University of Minnesota, Minneapolis, MN., 55455.

WE7. (3:15)

PERTURBATIVE APPROXIMATIONS IN THE ANALYSIS OF FUNDAMENTAL BANDS OF SPHERICAL-TOP MOLECULES

B. J. KROHN AND J. K. G. WATSON

To calculate high-J fine-structure lines in fundamental bands of spherical tops, one can usually replace the diagonalization of the Hamiltonian by a second- or third-order approximation. The new formalism uses an expansion in powers and products of the diagonal $F^{(4)}$- and $F^{(6)}$-coefficients of Moret-Bailly.[1] The fit to diode spectra attains about the same accuracy as the analysis that incorporates diagonalization, and the sets of derived parameters agree closely in value. Results will be discussed for the fundamental bands of SiF_4, where the theory converges rapidly for the ν_3 band and more slowly for the ν_4 band.

[1] J. Moret-Bailly, J. Mol. Spectrosc. 15, 344-354 (1965).

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Address of Watson: Herzberg Institute of Astophysics, National Research Council of Canada, Ottawa K1A 0R6, Canada.

WE8. (3:32)

DIODE AND DIFFERENCE-FREQUENCY LASER SPECTRA OF CUBANE

A. S. PINE, A. G. MAKI, AND A. G. ROBIETTE

Two of the three infrared-active fundamentals of cubane (C_8H_8) have been studied at near-Doppler-limited resolution using tunable laser instruments. The complete spectrum of the C-H stretching band, ν_{10}, near 2990 cm^{-1} was recorded with a difference-frequency system. The rotational structure of this band is extremely complex, indicating a strong second-order Coriolis resonance with a close-lying A_{2u} vibration. Portions of the C-C stretching band, ν_{12}, near 852 cm^{-1} were recorded with a diode laser. The structure in this band is much simpler, allowing for its analysis as a relatively unperturbed spherical top fundamental. The diagonal F4 approximation fits the R(45) to P(16) region to within the Doppler width, but off-diagonal corrections are indicated for higher J P-branch lines.

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WE9. (3:44)

ORDER, DISORDER, AND CLUSTERING IN ROTOR SPECTRA: A COMPARISON OF SPHERICAL AND ASYMMETRIC TOP DYNAMICS.*

W. G. HARTER, AND C. W. PATTERSON

The techniques used to elucidate spherical top spectral clustering effects[1] can be applied to other types of polyatomic molecules including those of low symmetry. Dynamical effective energy surfaces[2,3] can be drawn using the molecular constants in a general rotor Hamiltonian, and the surfaces can be used to calculate and understand the spectra and dynamics of the rotors. Spectral clustering effects such as rotational mixing of nuclear spin species are possible in asymmetric top XY_2 molecules as well as in the spherical tops XY_4 and XY_6.[1,3,4] The energy surfaces provide simple ways to calculate, predict, or rule out many such effects for a wide range of molecular species. We hope to show these surfaces in 3-D.

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*Research supported in part by NSF grant PHY-8207150.

[1] W. G. Harter, C. W. Patterson, and F. J. daPaixao, Rev. Mod. Phys. 50, 37(1978).
[2] W. G. Harter and C. W. Patterson, J. Math. Phys. 20, 1453(1979).
[3] W. G. Harter, Phys. Rev. A24, 192(1981).
[4] J. Borde, Ch. J. Bordé, C. Salomon, A. Van Lerberghe, M. Ouhayoun, and C. D. Cantrell, Phys. Rev. Lett. 45, 14(1980).

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WE10. (4:01)

HIGH VIBRATIONAL OVERTONES OF SPHERICAL TOP MOLECULES

C. W. PATTERSON AND W. G. HARTER

We give both a quantum and classical description of the high overtones of spherical top molecules using a generic three dimensional potential surface for the dipole active mode. This potential gives rise to quasi-periodic vibrational "clusters" as well as chaotic motion for various anharmonicities and energies. We hope to show the relevant vibrational trajectories in 3-D.

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WE11. (4.1E)

COMPARISON OF THE SYMMETRIZED CARTESIAN AND ANGULAR MOMENTUM BASIS SETS TO DESCRIBE VIBRATIONALLY EXCITED STATES IN SPHERICAL TOP MOLECULES

Harold B. Levene and David S. Perry

Analysis of the $3\nu_3$ band in two spherical tops, SF_6[1] and SiF_4[2], has shown that the cartesian basis is an appropriate description for this band in the octahedral case, while the tetrahedral case is adequately represented by the angular momentum basis. Using spectroscopic constants derived from force field analyses, the F_{1u}/F_2 subblocks of the vibrational Hamiltonian matrices of the bands of four vibrational quanta and one band of five quanta, $2\nu_2 3\nu_3$, are diagonalized in each basis set for both SF_6 and CF_4 to extend the comparison to more general vibrational levels.

Both bases fail to adequately describe CF_4. Examination of the relative quality of the various angular momentum and cartesian quantum numbers suggests a hybrid basis as a better representation of the tetrahedral case.

SF_6 is poorly described by the angular momentum basis. Within a vibrational band of SF_6, only a component whose vibrational motion lies along a single cartesian axis is well described by the cartesian basis. It is the lowest energy component, well separated in energy from the remaining components because of the single bond anharmonicity. Overtone spectroscopy was performed with an optical parametric oscillator in the region 2800 - 4200 cm^{-1}. Only components well described by the cartesian basis have measureable oscillator strength.

1 C. W. Patterson, B. J. Krohn and A. S. Pine, J. Mol. Spectrosc. 88(1) 133-166 (1981).

2 C. W. Patterson and A. S. Pine, J. Mol. Spectrosc. 96(2) 404-421 (1982).

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WE12. (4:35)

GENERAL HARMONIC FORCE FIELD FOR HYDROGEN PEROXIDE

J. J. HILLMAN AND J. D. ROGERS

An iterative finite difference method has been employed to compute the complete harmonic force field of H_2O_2. The derived force constants are in essential agreement with previous calculations(1) using Pulay's force method. This suggests that the chosen configurations are well suited to determining the potential energy function of H_2O_2. Scaling the ab initio force field results in a good overall fit to the frequencies of H_2O_2 and D_2O_2. The interaction force constants involving the torsional mode are all calculated to be quite small, in agreement with our earlier assumption(2) that these interaction force constants are zero.

[1] P. Botschwina, W. Meyer, and A. M. Semkow, Chem. Phys. 15, 25 (1976).

[2] J. D. Rogers and J. J. Hillman, J. Chem. Phys. 75, 1085 (1981); J. Chem. Phys. 76, 4046 (1982).

Address of Hillman: Infrared and Radio Astronomy Branch, NASA/Goddard Space Flight Center, Greenbelt, Maryland 20771.

Address of Rogers: Environmental Science Department, General Motors, Research Laboratories, Warren, Michigan 48090.

WE13. (4:47)

EFFECTS OF A PERTURBATION ON THE GROUND TORSIONAL-VIBRATIONAL STATE OF HYDROGEN PEROXIDE

WM. BRUCE OLSON AND ROBERT HUNT

Assignments have been made in the sub-bands of the symmetric and antisymmetric stretching vibrations of hydrogen peroxide arising from rotational levels of the ground torsional state with K quantum number equal to 8. The ground state energy levels are markedly affected by an interaction with levels of the first excited torsional state with K equal to 6. Assignments made in the antisymmetric stretching hot band, up to K equal to 8, confirm this interpretation. This perturbation has lesser, but still significant effects on other K values of the ground torsional state, and will require some revision of the ground state rotational constants recently determined from extensive submillimeter data[1,2].

[1] W. C. Bowman, F. C. DeLucia, and P. Helminger, J. Mol. Spectrosc. 87, 571-574 (1981).

[2] John J. Hillman, J. Mol. Spectrosc. 95, 236-238 (1982).

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Address of Olson: Molecular Spectroscopy Division, National Bureau of Standards, Washington, D.C. 20234.

WF1. (1:30)

OBSERVATION OF THE C(3/2) ← X(1/2) TRANSITION IN XeF

H. HELM, D. L. HUESTIS, M. J. DYER, AND D. C. LORENTS

$XeF(X_{v''})$, produced by KrF laser photodissociation of XeF_2, is excited by a doubled dye-laser to $XeF(B_{v'})$ and $XeF(C_{v'})$ and the broad-band B → A and C → A fluorescence is detected. The B and C states are distinguished by their differing decay rates at low pressure. Through its fluorescence excitation spectrum the C ← X transition is observed for the first time. The vibrational analysis of the C-X bands locates the C(v'=0) level at 775 cm^{-1} below the B(v'=0) level, and yields the first experimental vibrational constants for the C state (ω_e = 346 cm^{-1} and $\omega_e x_e$ = 2.2 cm^{-1}). A bandshape analysis of the C-X bands suggests that the equilibrium internuclear separation of the C state lies around 2.45 Å. Vibrational relaxation and vibrationally resolved collision-induced dissociation of $XeF(X_{v''})$ are also observed.

Supported by the Defense Advanced Research Projects Agency under contract N0014-80-C-0506, through the Office of Naval Research.

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WF2. (1:45)

PHOTOFRAGMENT SPECTROSCOPY OF Cs_2^+

H. HELM, R. MÖLLER, P. C. COSBY, AND D. L. HUESTIS

The electronic structure of Cs_2^+ has been investigated by photodissociation of fast molecular ions (formed by field ionization from a liquid cesium droplet) using dye lasers and fixed frequency lines from argon and krypton ion lasers covering portions of the wavelength range between 406 and 950 nm. The nature of the electronic transitions is characterized through analysis of their dependence on wavelength, polarization, and photofragment energy. Bound-free transitions from the ground $X^2\Sigma_g^+$ state to $1^2\Sigma_u^+$ (near 950 nm) and to $2^2\Sigma_u^+$ and $2^2\Pi_u$ (406 to 530 nm) are observed, as well as predissociated bound-bound transitions to $1^2\Pi_u$ (770 to 810 nm). In the latter case a spin-orbit splitting of 280 cm^{-1} is resolved.

Supported by NSF Grant No. PHY 8112534

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WF3. (2:00)

ROTATIONAL BRANCH STRENGTHS FOR $O_2(A^3\Sigma_u^+ \leftrightarrow X^3\Sigma_g^-)$

D. L. HUESTIS AND T. G. SLANGER

The forbidden $A^3\Sigma_u^+ \leftrightarrow X^3\Sigma_g^-$ transition in O_2 consists of the expected 13 rotational branches[1] but with relative intensities that are difficult to explain with simple single-perturber formulas.[2] To permit satisfactory simulation of this important transition in nightglow emission spectra we have developed a model that assumes spin-orbit mixing of $B^3\Sigma_u^-$ with $A^3\Sigma_u^+$ and spin-orbit and rotational mixing of $1^3\Pi_g$ with $X^3\Sigma_g^-$. Destructive interference between approximately equal contributions of $^3\Sigma_u^-$ and $^3\Pi_g$ is required to suppress the calculated O- and S-form branch intensities. Simultaneous spin-orbit and rotational mixing of $^3\Pi_g$ is required to adjust the relative intensities of the Q-form branches.

1. G. Herzberg, Can. J. Phys. 30, 185 (1952).
2. R. D. Present, Phys. Rev. 48, 140 (1935).

Supported by NSF Grant ATM-8011954.

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WF4. (2:18)

INTENSITIES OF FORBIDDEN BAND SYSTEMS OF MOLECULAR OXYGEN

C. M. L. KERR AND J. K. G. WATSON

The three Herzberg systems of absorption bands of oxygen in the region of 40 000 cm^{-1} correspond to orbitally forbidden transitions to the states $c^1\Sigma_u^-$, $A'^3\Delta_u$ and $A^3\Sigma_u^+$ from $X^3\Sigma_g^-$. These transitions acquire their intensity from allowed transitions by spin-orbit coupling. This study is concerned with
(a) the representation of the branch intensities of recent observations[1] of these forbidden bands by a set of transition moment parameters, and
(b) the relation of these transition moments to those of the allowed transitions through the spin-orbit matrix elements.

[1] B. Coquart and D. A. Ramsay, in preparation.

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WF5. (2:35)

PULSED LASER EXCITATION AND PHOTOACOUSTIC DETECTION OF THE 1-0 OXYGEN SCHUMANN-RUNGE BAND

P. B. KELLY, R. COHEN, R. B. MILES, AND J. GELFAND

Direct excitation into the 1-0 band of the molecular oxygen Schumann-Runge system has been achieved. Raman shifted fourth harmonic of a Nd:YAG laser was the excitation source. The laser was scanned over lines at the band origin by means of an intracavity etalon. The photoacoustic system used to detect the pulsed excitation will be described.

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WF6. (2:47)

HIGH RESOLUTION ABSORPTION CROSS SECTIONS AND BAND OSCILLATOR STRENGTHS OF THE SCHUMANN-RUNGE BANDS OF O_2

K. Yoshino, D.E. Freeman, J.R. Esmond, and W.H. Parkinson

Cross sections of O_2 at 300 K have been obtained from photoabsorption measurements at various pressures throughout the wavelength region 179.3 - 201.5 nm with a 6.65 m photoelectric scanning spectrometer equipped with a 2400 line/mm grating and having an instrumental width (FWHM) of 0.0013 nm. The measured absorption cross sections of the Schumann-Runge bands (12,0) through (1,0) in this wavelength region are absolute, i.e., independent of the instrumental width, a result not achieved previously. The measured cross sections will be presented graphically. Band oscillator strengths of the (12,0) through (1,0) bands have been determined by direct numerical integration of the measured cross sections.

Preliminary results of cross sections at 77 K will be discussed.

This work is supported by NASA Grant NSG 5176 to Harvard College.

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WF7. (3:15)

INTRACAVITY LASER ABSORPTION SPECTROSCOPY - A COMPARISON WITH CLASSICAL ABSORPTION - LINE SHAPES AND QUANTITATIVE MEASUREMENTS

M. Chenevier, M. A. Melieres, F. Stoeckel

Using a CW dye laser for intracavity laser absorption spectroscopy (ICLAS) with a controlled time generation and a time-resolved spectrum, we show that intracavity absorption follows the Lambert Beer Law.

By comparing the absorption of the very weak γ band of O_2 $b^1\Sigma_g^+(v'=2) \leftarrow X^3\Sigma_g^-(v''=0)$ in ICLAS and in multi-pass cell technique[1] we confirm that the intracavity technique gives reproducible results under different experimental conditions and is a highly sensitive quantitative method for measuring absolute absorption coefficients and collision broadening coefficients. This method does not necessitate any previous scaling in contrast with other sensitive methods like photoacoustic or optogalvonic techniques.

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1 J. J. Miller, L. P. Giver, R. W. Boese, J.Q.S.R.T. 16 (1976) 595.

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WF8. (3:27)

TIME EVOLUTION OF SHORT-LIVED MOLECULAR SPECIES OBSERVED BY INTRACAVITY LASER ABSORPTION SPECTROSCOPY

F. Stoeckel, M. D. Schuh and G. H. Atkinson

We report the feasibility of using CW intracavity laser absorption spectroscopy (ICLAS)[1] as a probe in detecting transient species generated by pulsed laser photolysis. The method of detection uses a time-generated CW laser beam and time-resolved spectra which are delayed with respect to the photolysis pulse. Variable time delays and a constant generation time have been used to detect the time dependence of the absorbing species at times as short as a few microseconds.

We applied the technique to the study of the time evolution of the formation of the free radical HCO generated by photolysis of gas-phase acetaldehyde (CH_3CHO) at pressures down to tens of mtorr.

We have also found that the ultimate sensitivity of the ICLAS technique is limited mainly by the mechanical stability of the cavity.

[1] M. Chenevier, M. A. Melieres, F. Stoeckel, to be published

[2] G. H. Atkinson, A. H. Laufer and M. J. Kurylo, J. Chem. Phys. 59 (1973) 350.

[3] G. H. Atkinson, T. N. Heimlich and M. W. Schuyler, J. Chem. Phys. 66 (1977 5005.

[4] A. J. Gill and G. H. Atkinson, Chem. Phys. Letters, 64 (1979) 426.

[5] R. J. Gill, W. D. Johnson and G. H. Atkinson, Chem. Phys. 58 (1981) 29.

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Address of M. Schuh: Department of Chemistry, Davidson College, Davidson, NC, 28036, USA.

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WF9. (3:44)

TIME-RESOLVED PHOSPHORESCENCE SPECTRA OF ACETALDEHYDE (CH_3CHO) AND PERDEUTEROACETALDEHYDE VAPORS

M. D. SCHUH, S. SPEISER and G. H. ATKINSON

The phosphorescence ($T_1 \rightarrow S_0$) spectra of vapor phase CH_3CHO and CD_3CDO were measured by time-resolved methods following pulsed (8ns) laser excitation at 320nm. The time-resolved phosphorescence is characterized by its radiative lifetime (23μs at 10 torr), its frequency shift (~2100 cm^{-1}) to lower energy from the onset of fluorescence, extensive vibronic structure, and rate of quenching by O_2. The observed vibronic structures and triplet-state lifetimes were distinctly different for CH_3CHO and CD_3CDO. The relationship between these phosphorescence spectra and those observed by energy transfer techniques is discussed. These results are also used to compare the phosphorescence spectra of acetaldehyde and other alkyl ketones and aldehydes, and to comment on the energy separations between S_1 and T_1 for CH_3CHO, vibronic assignments, and role of biacetyl in acetaldehyde photochemistry.

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WF10. (3:56)

IDENTIFICATION OF THE nf COMPLEXES IN N_2 BY UV ABSORPTION

E.S. CHANG AND K. YOSHINO

Absorption features at λ = 824, 815, and 810Å are identified as the 5f, 6f, and 7f complexes in molecular nitrogen. Our study of the 7f complex at 810Å shows that the main lines are separated by 4B ($B \approx 2$ cm^{-1}) rather than 2B and can be labeled as members of the O and the S branches. Theoretical analysis in terms of the frame transformation theory[1] yields line positions and strengths similar to the ℓ complex theory.[2] Generally excellent agreement is found between theory and experiment.

This work was supported by the Air Force under AFGL Contract #F19628-81-K-0007.

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[1] E.S. Chang and U. Fano, Phys. Rev. A 6, 173 (1972)

[2] Ch. Jungen and E. Miescher, Can. J. Phys. 47, 1769 (1969).

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Address of Yoshino: Center for Astrophysics, Harvard University, Cambridge, Massachusetts 02138, U.S.A.

WF11. (4:11)

ANALYSIS OF THE 5g-4f EMISSION LINES IN H_2

E.S. CHANG, C. PULCHTOPEK, AND E.E. EYLER

We re-examine the 5g-4f emission data in H_2 reported by Herzberg and Jungen[1] in light of our theory reported in the Thirty-seventh Symposium.[2] While we agree with their assignment of most of the lines, we believe that some weaker lines belong to higher vibrational states of the H_2^+ core. A new analysis of the line intensities suggests a much lower rotational temperature, perhaps 100° K instead of the reported 250° K. The dependence of the intensities on vibration will also be discussed.

This work was supported by the Air Force under AFGL Contract #F19628-81-K-0007, and in part by NSF PHY80-26547.

---

[1] G. Herzberg and Ch. Jungen, J. Chem. Phys. 77, 5876 (1982).

[2] E.S. Chang, 37th Symposium on Molecular Spectroscopy, Ohio State University, June 14-18, 1982, p. 90.

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WF12. (4:20)

ROTATIONAL ANALYSIS OF THE $B^1\Sigma^+ - A^1\Pi$ SYSTEM OF $^{13}C\,^{18}O$*

C. V. V. PRASAD, G. L. BHALE+, AND S. PADDI REDDY

The $B^1\Sigma^+ - A^1\Pi$ (Ångström) band system of the $^{13}C^{18}O$ molecule in the region 4100 - 6500 Å, excited in the anode column of a hollow cathode discharge tube of special design, was recorded. Out of a total of ten bands observed, the 1-0, 1-1, 0-0, 0-1, 0-2, 0-3, 0-4, and 0-5 bands were photographed under high dispersion and the rotational analyses of these except the complex 0-0 band carried out. Perturbations observed in the vibrational levels v = 0, 3 and 5 of the $A^1\Pi$ state were analyzed and information concerning the perturbing electronic states $a'^3\Sigma^+$ and $e^3\Sigma^-$ was obtained. The derived rotational constants (in cm^{-1}) of the A and B states can be represented by the following expressions:

$$A^1\Pi: \quad B_v = 1.4660 - 0.0201\,(v+\tfrac{1}{2}).$$

$$B^1\Sigma^+: \quad B_v = 1.7805 - 0.0219\,(v+\tfrac{1}{2}).$$

Other molecular constants derived from the analysis will be also discussed.

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*Research supported in part by NSERC Grant No. A-2440.

+G. L. Bhale is on leave from the Bhabha Atomic Research Centre, Bombay, India.

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WF13. (4:40)

TWO PHOTON EXCITATION OF THE $D^1\Delta - X^1\Sigma^+$ TRANSITION IN CO

C. KITTRELL, S. CAMERON, R.F. BARROW, L. BUTLER, AND R.W. FIELD

A frequency doubled pulsed dye laser is used to promote two-photon excitation of the $D^1\Delta - X^1\Sigma^+$ transition in carbon monoxide. Collisional transfer to $A^1\Pi$ leads to ultraviolet fluorescence which is detected with a solar blind photomultiplier. Rotationally resolved structure belonging to bands of three isotopically substituted molecules has been measured relative to the visible spectrum of iodine. Several vibrational bands up to v' = 12 have been analyzed and these data, combined with Simmons and Tilford's[1] values for v' = 1, give the molecular constants. Preliminary values for ^{12}CO are: T_e = 65,975.8(5); ω_e = 1061.7(3); $\omega_e x_e$ = 9.86(4); B_e = 1.259(4); D_e = 7×10^{-6}; α_e = .018(1) (all cm^{-1}).

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[1] J.D. Simmons and S.G. Tilford, J. Chem. Phys. 45, 2965 (1966).

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Address of Butler: Materials and Molecular Research Division, Lawrence Berkeley Laboratory and Department of Chemistry, University of California, Berkeley, California 94720.

WG7. (4.53)

OPTICAL STARK EFFECTS IN THE STIMULATED RAMAN SPECTRUM OF O_2*

R. A. HILL, A. OWYOUNG, and P. ESHERICK

Nonresonant optical Stark effects are observed in the high resolution ($0.002\ cm^{-1}$) stimulated Raman spectra of the pure spin, rotational, and vibrational bands of O_2 at focused pump laser intensities >3 GW/cm^2. Differences between the polarized and depolarized Raman spectra arise since the magnetic quantum number selection rules $\Delta M_J = 0$ and $\Delta M_J = \pm 1$ apply, respectively. Optical Stark effects in $^3\Sigma$ molecules (e.g., oxygen) differ somewhat from that observed for $^1\Sigma$ molecules (nitrogen) because of inversion of the $M_J = 0$ and 1 sublevels of the $(J,N) = (1,1)$ rotational state. Further, identical shifts of the $M_J = 1$ sublevels of the (1,1) and (2,1) rotational states result in polarized $^OP(2,1)$ and $^OR(1,1)$ lines that exhibit no second order optical Stark effect.

* This work is supported by the U.S. Department of Energy.

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WH1. (1:30)

ROTATIONAL RELAXATION AND Λ COMPONENT SWITCHING COLLISIONS IN THE BaO $A'\,^1\Pi$ STATE

YEN CHU HSU AND J. GARY PRUETT

Time delayed optical-optical double resonance is used to follow the rotational level and Λ component population in the $A'\,^1\pi$ state following single rotational and Λ component excitation. Fast rotational relaxation of small ΔJ is accompanied by slower Λ component changing processes with weak ΔJ propensities.

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WH2. (1:47)

QUENCHING OF THE $A^2\Sigma^+$ STATE OF OH AT ~1100 K

PAUL W. FAIRCHILD, GREGORY P. SMITH, AND DAVID R. CROSLEY

Rate constants for collisional quenching of the v'=0 level of the $A^2\Sigma^+$ state of the OH molecule have been measured at temperatures in the range 1000-1400 K. The OH was produced at these temperatures by a laser pyrolysis method,[1] in which a mixture of SF_6, H_2O_2 and the collision partner was irradiated by a pulsed CO_2 laser. The SF_6 absorbed the infrared radiation, rapidly heating the mixture and pyrolyzing the peroxide to OH radicals. The OH was pumped to the N'=6, J'=6 1/2, v'=0 level of the $A^2\Sigma^+$ state by a 10 nsec-long frequency doubled dye laser pulse fired 30 μsec after the CO_2 laser. Quenching rate constants were measured by the added gas pressure dependence of the fluorescence decay time.

The results, given as thermally averaged cross sections ($\AA^2$) at 1100 K are:

CO^*	H_2O^*	CH_4	NH_3	O_2^*	H_2^*	NO	N_2O	N_2^*	SF_6	CO_2^*
21	36	16	43	12	11	28	34	0.7	0.14	13

No significant temperature dependence was observed over the limited range covered, in agreement with expectations. However, the values are lower than room temperature literature values (which exist for colliders marked with an asterisk), except for H_2. The values for N_2 and SF_6 are conspicuously low.

Cross sections have been calculated with a collision complex model, where multipole attractive forces and a repulsive rotational barrier dominate the potential, a reformulation of an approach used for SO_2.[2] The experimental results for the first eight of the collision partners listed agree well (±25%) with the calculation, assuming 0.45 probability of quenching per capture collision.

This research was supported by the U.S. Army Research Office.

1 P. W. Fairchild, G. P. Smith and D. R. Crosley, Nineteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1983, in press.
2 D. L. Holtermann, E.K.C. Lee and R. Nanes, J. Chem. Phys. 77, 5327 (1982).

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WH3. (2:04)

INTRAMOLECULAR VIBRATIONAL REDISTRIBUTION AS SEEN IN TIME RESOLVED EMISSION FROM p-DIFLUOROBENZENE

K.W. Holtzclaw, D.A. Dolson and C.S. Parmenter

Time resolved fluorescence spectra are being obtained from several vibrational levels in S_1 p-difluorobenzene using the technique of chemical timing.[1] In this method varying pressures of the efficient electronic state quencher oxygen are used to restrict the fluorescence lifetime of the molecule to as little as 10 ps. Spectra taken in the presence of sufficient pressures of oxygen show a reduction in the fraction of emission which is structureless, an indication of incomplete IVR. These spectra are interpreted using kinetic models grounded in the predictions of the intermediate and statistical limit cases of radiationless transition theory.[2,3] At present it has been found that the intermediate case kinetics best fit data for the $3^1 5^1$ (ϵ_{vib} = 2069 cm^{-1}) and $3^1 5^1 30^1$ (ϵ_{vib} = 2191 cm^{-1}) levels with IVR rates on the order of 1 ns and 50 ps respectively.

1. R.A. Coveleskie, D.A. Dolson, C.S. Parmenter, J. Chem. Phys. 72, 5774 (1980).

2. F. Lahmani, A. Tramer, and C. Tric, J. Chem. Phys. 60, 4431 (1974).

3. K. Freed, A. Nitzan, J. Chem. Phys. 73, 4765 (1980).

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WH4. (2:21)

FLUORESCENCE SPECTRA OF p-DIFLUOROBENZENE IN A MOLECULAR BEAM, EVIDENCE FOR ROTATIONAL INVOLVEMENT IN INTRAMOLECULAR VIBRATIONAL REDISTRIBUTION

S.H. Lee and C.S. Parmenter

Examples of single vibronic level (SVL) fluorescence spectra displaying congestion exceeding that expected from thermal inhomogeneous broadening are abundant and have been used as evidence for intramolecular vibrational redistribution (IVR). Based on the congestion observed in SVL spectra, the onset of the IVR process has been shown to occur at low vibrational energies in the first excited singlet state where the vibrational density of states is on the order of unity. In order to account for the observed congestion, rotational involvement in IVR has been suggested as a means of coupling a larger number of vibronic levels. By comparing SVL spectra of p-difluorobenzene obtained at room temperature with those obtained in the cold conditions of a molecular beam, we have found evidence for rotational involvement in IVR. In the molecular beam the spectra observed show less congestion than the equivalent room temperature spectra, indicating that the onset of IVR occurs at higher vibrational energy in the low temperature case.

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WH5. (2:33)

INTERMOLECULAR POTENTIALS AND VIBRATIONAL ENERGY FLOW IN LIQUIDS: V-T RELAXATION OF CO(v=1) BY H_2, D_2 AND He IN LIQUID Ar.

Donald W. Lupo and G.E. Ewing

The rate constants for collisional deactivation of the v=1 level of CO by H_2, D_2 and He dilute in liquid Ar were measured using chopped blackbody excitation and signal-averaged detection of IR fluorescence decay. The ratios of the rate constants in the liquid phase to those for the same processes in the gas phase[1] (k_l/k_g) were found to be ~ 1.1, 0.8 and 1.6 for CO-H_2, CO-D_2 and CO-He, respectively.

These results do not agree well with most of the available models for vibrational relaxation in liquids, which predict that k_l should be several times k_g. It is proposed that changes in the effective intermolecular potential introduced when the collision partners are put into solution lower the probability of energy transfer, and consequently the rate constant, when the mean kinetic energy is comparable to or smaller than the attractive energy between the interacting species.

1. M. Matti Maricq and C.J.S.M. Simpson, Chem. Phys. Lett., (to be published).

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WH6. (2:55)

VIBRATIONAL ENERGY TRANSFER OF CO BY CH_4, CD_4, AND CF_4 IN LIQUID Ar

H.M. Abdel-Halim and G.E. Ewing

The rate constant for the vibrational relaxation of CO(v=1) by CH_4, CD_4, and CF_4 were measured in liquid Ar. A comparison has been made with the gas phase results measured at the same temperature[1], which enables us to test the validity of the Isolated Binary Collision (IBC) model.

A blackbody source was used to excite CO to the v=1 level. The fluorescence emission from the excited CO was used to monitor the transfer of vibrational energy in the system. Several concentrations of CO and its collision partner were studied, from which the rate constant could be extracted.

Our results show that the liquid phase rate constant (k_l) is almost equal to the gas phase one (k_g), where the IBC model predicts k_l to be several times larger than k_g. However, within an order of magnitude accuracy the IBC model is still valuable.

[1] J.M. Jackson, P.A. Lewis, M.P. Skirrow, and C.J.S.M. Simpson, Trans. Faraday Soc. II, 75, (1979) 1341.

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WH7. (3:12)

DIODE INFRARED LASER DOUBLE RESONANCE OF SUBSTITUTED METHANES: SPECTROSCOPY AND RELAXATION[1]

J.I. STEINFELD, D. HARRADINE, L. LAUX, AND M. DUBS

The $\nu_5 \leftarrow 0$ and $2\nu_5 \leftarrow \nu_5$ transitions in CDF_3 have been investigated by Diode-Infrared Laser-DOuble Resonance. Two-, three-, and four-level double-resonance and AC-Stark-modulated signals have been observed. Analysis of these spectra yeilds considerably improved molecular constants. Time-resolved measurements of rotational energy transfer indicate that the cross-section for self-relaxation is approximately fourteen times gas-kinetic, and that neighboring levels are populated with dipole-like ($\Delta J = \pm 1$, $\Delta K = 0$) propensity rules. Preliminary results on $^{13}CD_4$ will also be reported.

[1]Supported by National Science Foundation Grant CHE81-09963.

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WH8. (3:29)

PHONON-ASSISTED ENERGY TRANSFER IN MOLECULAR CRYSTALS

I. Y. CHAN AND M. P. KARNETT

Phonon-assisted triplet energy transfer in molecular crystals is investigated with the technique of laser line-narrowing. Benzophenone (BP) in BP-d_{10} and 4,4' dibromodiphenyl ether (DDE) have been selected as examples. A narrow-band pulsed dye-laser excites a subset of the molecular sites, leading to narrow phosphorescence emission at 2 K. As energy transfer occurs at higher temperature, the emission line broadens. Analysis of the temporal evolution of the spectral profile in the Inokuti-Hirayama region[1] provides a measurement of the energy transfer rate. The temperature dependence of such rates reveals the mechanism of phonon interaction with the molecular excited state.[2] Experimental results will be discussed in view of the increased low frequency phonon population in a soft molecular crystal.

[1]M. Inokuti and F. Hirayama, J. Chem. Phys. 43, 1978 (1965).
[2]S. K. Lyo, T. Holstein and R. Orbach, Phys. Rev. B18, 1637 (1978).

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WH9. (3:46)

DIRECT OBSERVATION OF INTRAMOLECULAR ENERGY REDISTRIBUTION IN p-DIFLUOROBENZENE BY PICOSECOND GATING

R. MOORE, F.E. DOANY, E.J. HEILWEIL and R.M. HOCHSTRASSER

Results are presented on the picosecond time evolution of the fluorescence spectrum of p-difluorobenzene under collision free circumstances. Time-resolved single vibronic level emission spectra were obtained by the technique of frequency down-coversion by non-linear mixing of the molecular fluorescence with a picosecond laser pulse in a non-linear gating crystal. High resolution down-coverted spectra were obtained by using a monochromator and photomultiplier tube; lower resolution down-converted spectra were obtained by using a spectrograph and a reticon array-based optical multichannel analyzer system. The time gated spectra consisted of structured emission corresponding to vibronic transitions superimposed on a diffuse background. The diffuse background displayed a time evolution that differed from that of the structured region of the spectrum. The observed kinetics might mean that intramolecular rovibrational energy redistribution is occuring on a timescale of ca. 6 ps.

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WH'1. (4.05)

CHEMILUMINESCENT OXIDATION OF ZINC ATOMS BY NITROUS OXIDE

Brian G. Wicke

The chemiluminescent oxidation of zinc atoms by nitrous oxide to form ZnO* has been studied utilizing a laser vaporization pulsed beam source to produce the zinc reactant. The kinetic energy dependence of the chemiluminescent reaction cross section has a threshold at 1.6×10^{-19} joules/molecule (1.0 eV) in the center of mass; this threshold value has been used to estimate the dissociation energy of ZnO as $D \geq 4.48\times10^{-19} \pm 0.32\times10^{-19}$ joules [2.8 (±.2) eV)]. The reaction cross section increases with increasing kinetic energy in accord with the Arrhenius model from threshold to 3.2×10^{-19} joules (2.0 eV), but then increases more rapidly. Above threshold, small amounts of thermal energy added to the N_2O reactant increase the reaction cross section seventy times more than the equivalent energy supplied as relative kinetic energy. This energy selectivity is interpreted in terms of an electron jump reaction mechanism which is significantly enhanced by the ν_2 bending vibrational mode of N_2O.

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WH'2. (4:2?)

JET SPECTROSCOPY OF PERPROTONATED AND PERDEUTERATED BENZENE DIMERS BY 2-COLOR RESONANCE PHOTOIONIZATION

K. H. FUNG, H. L. SELZLE and E. W. SCHLAG

Benzene dimers (H-H, D-D, and H-D) from perprotonated (H) and perdeuterated (D) benzene are prepared in a seeded supersonic jet and are analyzed by a two-color resonance-enhanced two-photon ionization technique.[1] The experiment involves an excitation to the first electronic state S_1, (corresponding to $^1B_{2u}$ of the parent benzene monomer) by means of a tunable laser, and subsequent photoionization from this intermediate excited state with another proton. The ions produced are analyzed in a time-of-flight mass spectrometer.

Our results indicate that the excitation to the S_1 state is localized in either half of the dimer. In addition to the isotopic effect, an extra stabilization energy is found in both of the homo-dimers (H-H and D-D), which appears as a red shift in our spectra.

[1]K.H. Fung, W.E. Henke, T.R. Hays, H.L. Selzle and E.W. Schlag, J. Phys. Chem. 85, 3560 (1981).

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WH'3. (4:34)

FTIR SPECTRUM OF BENZENE IN A SUPERSONIC EXPANSION

D. SNAVELY, V. WALTERS, S. COLSON AND K. WIBERG

The 700cm^{-1} and 3050cm^{-1} region of benzene seeded in argon is studied using Fourier transform infrared absorption spectroscopy. Using a band contour analysis of the 700cm^{-1} region, the T_{rot} is determined to be 80 ± 15K. The assignments of the sequence hot band structure in this region is discussed. The T_{vib} is > 170K, which indicates a disequilibrium between the rotational and vibrational degrees of freedom.

In the 3050cm^{-1} region of the jet spectrum, the rotational envelopes for the three bands which make up the Fermi triad are separated. A band contour analysis, including Coriolis interaction, is used to study each band.

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WH'4. (4:51)

FTIR SPECTRUM OF PYRIDINE IN A SUPERSONIC EXPANSION

V. WALTERS, K. WONG, D. SNAVELY , S. COLSON AND K. WIBERG

Fourier transform infrared absorption spectroscopy was used to investigate the rotational and vibrational cooling of a 1:1 pyridine-argon mixture in a supersonic expansion. The C-H stretching bands in the 3000 cm^{-1} region and the C-H out-of-plane bend at 700 cm^{-1} were analyzed.

Band contour analysis of the 700 cm^{-1} band indicates a rotational temperature of 100±20 K. Consideration of the sequence band structure and isotope shifts for this band suggest a vibrational temperature of 140±40 K.

The spectrum of cooled pyridine was used by K. Wong et.al.[1] in the vibrational assignment of the fundamentals in the C-H stretching region. A rough band contour analysis confirms these assignments.

[1] K. N. Wong and S. D. Colson, submitted for publication.

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RA6.

FIRST INFRARED DETECTION OF ATMOSPHERIC NO_2 FROM THE GROUND

J.-M. FLAUD, C. CAMY-PEYRET, A. PERRIN, J. LAURENT AND G.M. STOKES

Up to now, infrared atmospheric NO_2 measurements have mainly been performed in the 6.2 μm region from aircraft or balloon. Indeed this spectral region covers the strongest infrared band of NO_2 which is ν_3. However, it is not possible for measuring NO_2 from the ground to work in this spectral region because the NO_2 absorption is hindered by the strong absorbing ν_2 band of water vapor. The second strongest absorbing band of NO_2 which is $\nu_1+\nu_3$ falls in the 3.4 μm region which is a relatively clear atmospheric window. However, since $\nu_1+\nu_3$ is about 20 times weaker than ν_3, it is necessary to have the best knowledge of the line parameters of the $\nu_1+\nu_3$ and $\nu_1+\nu_2+\nu_3-\nu_2$ bands of NO_2 to be able to recognize unambiguously the weak absorption peaks of this molecule in atmospheric spectra.

Using an hamiltonian which takes explicitly into account the Coriolis interaction between the $(v_1\ v_2\ v_3)$ and the $(v_1\ v_2+2\ v_3-1)$ vibrational states of NO_2, it has been possible to reproduce very satisfactorily the rotational levels of the interacting states (1 2 0),(1 0 1) and (1 3 0),(1 1 1). Also a least squares fit of the available experimental intensities of $\nu_1+\nu_3$ has provided us with the expansion of the transformed transition moment of this band which has then been used together with the wavefunctions resulting from the diagonalization of the hamiltonian matrix, to generate an improved set of line parameters for the $\nu_1+\nu_3$ and $\nu_1+\nu_2+\nu_3-\nu_2$ bands absorbing in the 3.4 μm region. This compilation has then been used to detect for the first time NO_2 absorption peaks in atmospheric spectra recorded from the ground. Thirteen well isolated features appearing clearly in high resolution Fourier transform atmospheric spectra recorded at Kitt Peak have allowed a precise determination of NO_2 vertical colum densities. Indeed from the analysis of 4 spectra recorded at air masses of 10.7, 5.4, 3.1 in the morning and of 10.8 in the afternoon, vertical column densities of 1.8 ± 0.3 and 3.25 ± 0.46 (in 10^{15} molecule cm^{-2}) have been derived for the morning and the evening.

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RA7.

Sub- Doppler Saturation Spectroscopy Using Microwave Sidebands on CO_2 Laser Lines: Hyperfine Structure in NH_3 and Vibration-Induced Dipole Moment in Tetrahedral Molecules

Gottfried Magerl, Joan M. Frye, Welf A. Kreiner, and Takeshi Oka

We report the observation of infrared Lamb dips using a widely tunable laser source. The microwave sidebands generated on CO_2 laser lines provide sufficient power (~0.5 mW) and spectral purity ($\Delta\nu \lesssim 100$ KHz) for saturation spectroscopy. This method is applied to observe the quadrupole hyperfine structure in the ν_2 fundamental band of NH_3 and to measure the vibration-induced dipole moment[1] in the ν_4 band of SiH_4 and the ν_3 band of SiF_4.

[1]M. Mizushima and P. Venkateswarlu, J. Chem. Phys. 21, 705 (1953).

RB2. (10:15)

OPTICAL AND MAGNETO-OPTICAL ROTATION DUE TO TRANSVERSE ELECTRONIC MOTION IN THICK HELICES OF NON-INTEGRAL TURNS. Samuel H. Brown and Ying-Nan Chiu

A three-dimensional arc coordinate system[1] is used to treat the electronic motion along a thick, instead of infinitely thin, helix. Extending the existing work on "one-dimensional" longitudinal motion along an infinitely thin helix, we have computed electronic dipole and magnetic dipole matrix elements involving transverse quantum numbers and covering integral as well as non-integral number of helical turns. The contribution of these transverse motions to optical and magneto-optical effects will be discussed.

[1] E. A. Power and T. Thirunamachandran, Proc. Roy. Soc. London A313, 403 (1969).

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RB3. (10:27)

"CRYSTAL FIELD" THEORY FOR THE RYDBERG STATES OF POLYATOMIC MOLECULES AND ORBITAL CORRELATION TO DISSOCIATED FRAGMENTS. Y. N. Chiu

Approximate energy expression of a Rydberg electron of given orbital angular momentum L is derived showing its m_L dependence. The derivation takes into account of multipole potential field up to hexadecapole and includes mixing of different L's by odd (dipole and octopole) potentials for systems without inversion symmetry. The proportion of different L's will be estimated from (translational) expansion[1] of atomic orbitals in the LCAO-MO'S. Symmetry constraints and correlation between Rydberg molecular orbitals and dissociated fragments will be discussed.

[1] see, for example, Y. N. Chiu, J. Math. Phys. 5, 283 (1964) and references therein.

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RB4. (10:44)

DEGENERATE STATES IN OPTICAL ROTATION. Ying-Nan Chiu

Optical rotation for random molecular systems is proportional to the second-order matrix element over the pseudoscalar operator $\mu \cdot m$. For inherently active molecules in non-degenerate ground states with charge density belonging to the totally symmetric irreducible representation, the pseudoscalar must also belong to this same representation. The present work will discuss the effect of degenerate ground as well as intermediate states. Possible matrix elements and symmetries involving various components of the degenerate set will be deduced using the irreducible tensor coupling coefficients.[1] The physical implication of these degeneracies will be discussed.

[1] J. S. Griffith, "The Theory of Transition-metal Ions" (Cambridge, 1961); The Irreducible Tensor Method for Molecular Symmetry Groups" (Prentice Hall, 1962).

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RB5. (10.55)

VALENCE BOND MODEL FOR $^1n\pi^*$ STATES OF 2,2',4,4'-TETRAMETHYLCYCLOBUTANE-1,3-DIONE (TMCBD)

W. R. WADT, W. R. MOOMAW AND S. M. JAFFE

The ultraviolet absorption spectrum of TMCBD has been interpreted in terms of four [R. Spafford, J. Baiardo, J. Wrobel and M. Vala, J. Am. Chem. Soc. 98, 5217(1976)] and three [R. D. Gordon, M. Caris and D. G. Newman, J. Mol. Spectrosc. 60, 130(1976)] low-lying $^1n\pi^*$ states. We report valence bond calculations, which emphasize the localized nature of the $n\rightarrow\pi^*$ excitations on the carbonyl oxygens. The results show that there are only two low-lying $^1n\pi^*$ states (1^1A_u and 1^1B_{1g}) with the next set (2^1A_u and 2^1B_{1g}) lying at least 3 eV higher. The spectra are reinterpreted in light of the valence bond calculations. Comparison with calculations on CBD reveals the important through-bond interactions induced by the methyl groups in TMCBD. Ionization from the oxygen lone pairs will also be considered.

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RB6. (11:13)

THE CONVERGENCE PROPERTIES OF MR-CI ENERGIES

F. B. BROWN, R. SHEPARD, AND I. SHAVITT

A series of Multi-reference Configuration Interaction (MR-CI) calculations has been undertaken to study the general convergence properties of MR-CI energies to the full CI energy. The Complete Active Space SCF (CASSCF) method has been used for determining the reference spaces and optimizing the molecular orbitals. Results will be reported for three points on a double-zeta, ground state potential surface of H_2O and an 80 orbital calculation on $(H_2)_2$. Comparisons to the full CI results and to a series of single-reference CI calculations will be presented. It will be shown that for these systems, the MR-CI method provides a balanced treatment of a potential surface.

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RB7. (11:25)

THEORETICAL STUDY OF CS_2 POTENTIAL SURFACE

R. N. DIFFENDERFER AND I. SHAVITT

The surface for dissociation of CS_2 to CS + S has been studied using ab initio MCSCF methods. Gaussian DZ+P basis sets were used, producing a ground state energy of -833.080247 for a 61 reference MCSCF wavefunction. The calculated dissociation energy, 4.38 eV, is in good agreement with experiment, 4.46 eV.

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RB8. (11:42)

STURMIAN BASIS MATRIX SOLUTION OF VIBRATIONAL POTENTIALS

E. YURTSEVER

The efficiency of a sturmian basis for solution of the one-dimensional Schrödinger equation is demonstrated.(1) The necessary one-electron integrals can be obtained as very simple analytical formulas. Eigenvalues are weakly affected by the non-linear parameter which simplifies the optimization problem.

Franck-Condon overlap integrals can also be computed relatively easily even for potentials which have different equilibrium bond lengths(2). Photoelectron transition probabilities for H_2 and N_2 obtained by this approach compare reasonably well with experimental data.

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[1] E.Yurtsever, O.Yılmaz and D.D.Shillady, Chem.Phys.Lett. 85, 111 (1982)
[2] E.Yurtsever, Chem.Phys.Lett. 91, 21 (1982)

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RC1. (3:30)

A VIBRATIONAL CIRCULAR DICHROISM (VCD) STUDY OF THE STEREOCHEMISTRY OF Co(III) AND Cr(III) COMPLEXES

DARYL YOUNG, FAY RATNOWSKY, SUSAN BECKER, ELMER LIPP, AND LAURENCE NAFIE

We have prepared a series of complexes, $M(en)_3X_3 \cdot nH_2O$, where M = Co(III), Cr(III), en = ethylenediamine, and X = $C\ell^-$, Br^-, I^-. The solution VCD of these complexes were measured in the NH and CH stretching regions on our dispersive instrument, and the NH and CH bending regions were examined on our Fourier Transform instrument. The spectra will be interpreted and the effects of ion-pair formation on the spectra will be discussed.

We will also show the VCD spectra for the complexes, $Co(acetylacetonato)_3$ and $Co(acetylacetonato)_2$(L-alaninato). Their spectra show the relative importance of the configuration, vicinal, and conformational contributions to the chirality observed in both the stretching and bending regions of their vibrational spectra.

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RC2. (9:47)

SOME TECHNICAL ASPECTS OF FTIR-VCD

E. D. LIPP AND L. A. NAFIE

Application of FTIR spectroscopy to vibrational circular dichroism (VCD) has effectively incorporated the Fourier advantages of increased sensitivity and superior resolution capabilities to these measurements. The purpose of this talk is to discuss some technical aspects of this technique which have been alluded to in the past but not thoroughly discussed. Specifically, we will discuss:

1) phase correction

2) resolution, particularly its effect on the size of the spectral features

3) absorption artifacts

We will also show some representative spectra down to 800 cm^{-1} in energy and at unprecedented S/N.

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RC3. (9:04)

RAMAN OPTICAL ACTIVITY IN THE SKELETAL MOTIONS OF (+)-(3R)-METHYLCYCLOHEXANONE

T. B. FREEDMAN, C. G. ZIMBA, W. ZUK AND L. A. NAFIE

The normal modes giving rise to the Raman optical activity (ROA) spectrum of (+)-(3R)-methylcyclohexanone in the region below 650 cm^{-1} have been assigned based on Raman spectra of the parent compound and five specifically deuterated isotopomers. Stereoprojections of the molecule displaced along the vibrational coordinates demonstrate that the low frequency normal modes and ROA fetures arise from deformation and torsional modes of the cyclohexane C_6 (D_{3d}) skeleton coupled to axial and equitorial motion of the carbonyl and methyl groups, and an additional methyl torsional mode.

Calculations of ROA intensity using the Raman atomic polar tensor model[1] will be presented and compared to experiment.

[1]T. B. Freedman and L. A. Nafie, J. Chem. Phys. 78, 27 (1983).

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RC4. (9:21)

VIBRATIONAL CIRCULAR DICHROISM OF SMALL MOLECULES

A. ANNAMALAI AND T. A. KEIDERLING

For trans-1,2-dideuteriocyclobutane vibrational circular dichroism has been measured in CCl_4 solution and localized molecular orbital calculations have been performed. The results are compared with previously reported gas phase and fixed partial charge spectra. A similar comparison for 1,3-dideuterioallene will also be made.

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RC5. (9:38)

COUPLED OSCILLATOR INTERPRETATION OF THE VCD OF DICARBONYL CONTAINING STERIODS

USHA NARAYANAN AND T. A. KEIDERLING

Vibrational circular dichroism spectra of several steroidal compounds containing two carbonyl groups on six-membered rings have been measured in the C=O stretching region. The results have been compared to the predictions of the degenerate coupled oscillator model. The sign and shape of the predicted spectra agree with the observed results in all but one case. The magnitudes generally agree to within a factor of two, with two exceptions. Attempts were made to correct the theory for misalignment of dipoles and non-degeneracy of the oscillators. In general, such corrections did not lead to an improved agreement.

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RC6. (10:10)

THE EFFECT OF DEUTERATION ON THE AMIDE I & II BANDS OF α-HELICAL POLYPEPTIDES AS EVIDENCED BY VCD STUDIES

A. C. SEN AND T. A. KEIDERLING

VCD spectra of some of the α-helical polypeptides, both normal and deuterated, have been recorded in the Amide I and Amide II region. The most striking effect of complete deuteration is the characteristic shift in absorption and VCD spectra as well as change in the VCD shape in some cases. The sign of VCD depends only on the sense of helicity of the α-helix, being not affected by deuteration. Attempts will be made to analyse the anomalies in the observed spectra.

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RC7. (10:27)

MAGNETIC VIBRATIONAL CIRCULAR DICHROISM OF METHYL HALIDES AND AMMONIA

T.R. DEVINE AND T.A. KEIDERLING

Absorption and magnetic vibrational circular dichroism (MVCD) of CH_3X (X = I, Br, Cl, F), and NH_3 in solution have been measured in the C-H and N-H stretching and bending regions. The results show MVCD dominated by monosignate B terms. The symmetric and asymmetric stretches have MVCD of opposite signs. Moment analysis indicates the magnitude of MVCD is greater in the E normal mode vibration than in the A_1; and that the magnitude increases with increasing halogen mass. These results will be discussed in light of various models of the origin of MVCD.

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RC8. (10:44)

SOME ASPECTS OF THE CIRCULAR DICHROISM MEASUREMENTS ON FOURIER TRANSFORM INFRARED (FTIR) SPECTROMETERS

D. F. MICHALSKA AND P. L. POLAVARAPU

Vibrational circular dichroism (VCD) measurements using FTIR techniques were reported recently.[1] In these measurements, the VCD spectra are obtained by subtracting the VCD measured for the two enantiomers of a chiral molecule. This is necessary to eliminate the base line artifacts and to determine the zero line of VCD spectra. This procedure however cannot be used when for a given optically active sample, (a). both enantiomers are not resolved (b). the enantiomers are not of same optical purity. Carbohydrates are one series of molecules for which both enantiomers are not available. We present a procedure to determine the zero line in such cases and discuss the experimental results. We also present the first VCD measurements below $900 cm^{-1}$.

[1] E. D. Lipp, C. Zimba and L. A. Nafie, Chem. Phys. Lett., 90, 1(1982).

Address of Michalska and Polavarapu: Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235.

RC9. (11:01)

FOURIER TRANSFORM INFRARED ABSORPTION AND CIRCULAR DICHROISM OF CARBOHYDRATES

D. M. BACK AND P. L. POLAVARAPU

Vibrational circular dichroism (VCD) studies on carbohydrates were undertaken recently[1] in C-H stretching region. Our investigations on carbohydrates are aimed at two different aspects. One is to identify the vibrational bands that are characteristic to different anomers in aqueous solutions. Second is to use this information to understand VCD in mid infrared region. The results obtained in our investigation using a Fourier transform infrared spectrometer will be presented.

[1] H. A. Havel, Ph. D. Thesis, University of Minnesota (1981).

Address of Back and Polavarapu: Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235.

RC10. (11:1?)

SPECTROSCOPIC MODULATION TECHNIQUES TO OBSERVE INFRARED SPECTRA FOR SPECIES IN THE ELECTRODE SOLUTION INTERFACIAL REGION

J. W. RUSSELL, A. BEWICK, AND J. OVEREND

Two spectroscopic modulation techniques have been adapted for studies of infrared spectra of species in the electrode solution interfacial region. Electrochemically modulated infrared reflectance spectroscopy, EMIRS, extends into the infrared the modulated specular reflectance technique previously used in the uv-visible region for identification of species produced during redox reactions in electrochemical cells. Infrared reflection absorption spectroscopy, IRRAS, previously utilized for studies of gas adsorbates on metals has also been successfully adapted for use with metal substrates under potentiostatic control and adsorbates from aqueous solution.

EMIRS utilizes a square wave modulation of the electrode potential in order to discriminate infrared absorptions by oriented species on or near the electrode surface from absorptions of bulk solution species. Using a spectroelectrochemical cell with a working electrode mirror positioned a few microns from an infrared window, sufficient infrared through-put is achieved while maintaining potentiostatic control for modulation frequencies of 10-500 cps. Sensitivity levels are such that spectra of submonolayer quantities of adsorbates with strong infrared bands are observable. Since EMIRS spectra are difference spectra between species present at the two selected modulation potentials, even strongly absorbing species whose surface concentrations, orientations, and spectra are potential independent or weakly dependent may not be observed. The complementary IRRAS method avoids this limitation.

IRRAS utilizes polarization modulation of the incident infrared radiation to make visible for surface species only vibrational modes with non-zero surface normal dipole derivatives. Although IRRAS has the advantage of retaining the electrode potential as a variable experimental parameter, the sensitivity levels achieved to date are less than those obtained using EMIRS.

Examples of spectra for CO, HSO_4^-, C_5H_5N, and H_2O using Pt, Rh, Ag, and Au electrodes will illustrate: (1) a strongly adsorbed molecule visible by EMIRS due to the potential dependence of its vibrational frequency, (2) a species whose surface concentration changes with variation in the electrode potential, (3) a species whose infrared intensity depends upon the electrode potential, and (4) a species whose structure is changed by changing the electrode potential.

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RC11. (11:35)

INFRARED SPECTROSCOPY OF PHYSISORBED MOLECULES ON ALKALI HALIDE SURFACES

C.A. Baumann, W.C. Schinzer and G.E. Ewing

Vaporization of alkali halides has been used to produce high surface area films which are transparent in the infrared.[1] Small molecules adsorbed on such surfaces in sub-monolayer coverages have been studied by infrared spectroscopy to characterize surface-adsorbate and/or adsorbate-adsorbate interactions[2]. We have observed coverage-dependent absorptions due to CO on 77K NaCl films, with features attributed to multiple sites at the surface. Other adsorbed molecules studied in our laboratory will also be discussed.

1. M. Folman and Y. Kozirovski, J. Coll. Interf. Sci. 38, 51 (1972) and references contained therein.

2. J. Heidberg, S. Zehme, C.F. Chen, and H. Hartmann, Ber. Buns. Ges. Phys. Chem. 15, 1046 (1971).

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RC12. (11:52)

BOND POLAR PARAMETERS FROM INTEGRATED INFRARED INTENSITIES

B. GALABOV

Infrared band intensities can be decomposed into molecular polar parameters. These parameters are used to characterize polar properties of the molecules and for prediction of vibrational intensities. In this work the theoretical aspects and some applications of a recently developed procedure[1] for parametric interpretation of IR intensities are discussed. The polar parameters used represent derivatives of the total dipole moment with respect to linear and angular coordinates describing vibrational displacements of individual valence bonds in a molecule. Some recent advances in the theoretical approach will be presented.

---

[1] B. Galabov, J. Chem. Phys. 74, 1599 (1981).

Address of Galabov: Department of Chemistry, University of Sofia, 1126 - Sofia, Bulgaria.

RE1. (1:30)

THEORY FOR VIBRATION-ROTATION-LARGE AMPLITUDE INTERNAL MOTION INTERACTIONS

C. RICHARD QUADE AND YUHUA GUAN

A theory for vibration-rotation-large amplitude motion interactions is being developed using curvilinear internal coordinates for the vibrational degrees of freedom. A modified Nielsen transformation is used to separate rotation from the 3N - 7 vibrations in zeroth order. Then the "R-transformation" is used to separate the 3N-7 vibrations from the large amplitude internal motion in the zeroth order kinetic energy. The approach is applicable to any molecular system where the principal axes of the equilibrium geometry do not change during the large amplitude motion.

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RE2. (1:47)

THE INTERNAL COORDINATE FORMULATION OF THE VIBRATION-ROTATION ENERGIES FOR SYMMETRIC TOP AND SPHERICAL TOP MOLECULES

WILLIAM B. CLODIUS AND C. RICHARD QUADE

The vibration-rotation Hamiltonians for the planar and non-planar XY_3 symmetric top and XY_4 and XY_6 spherical top molecules have been derived to second order using curvilinear internal coordinates for the vibrational degrees of freedom. Expressions for the anharmonic vibrational spectroscopic coefficients and the vibration-rotation spectroscopic coefficients have been obtained from the Hamiltonians. For these coefficients, the anharmonicities of both the rotational and vibrational kinetic energies have been derived from the molecular geometries for all of the types of molecules mentioned above. Quantative results have been obtained from application to some typical symmetric top and spherical top molecules.

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RE3. (2:04)

HIGHER-ORDER ℓ-DOUBLING OF LINEAR MOLECULES

James K. G. WATSON

The ℓ-doubling in the degenerate mode v_t of a linear molecule is of the form

$$\Delta F = q_t J(J+1) + q_t^J J^2 (J+1)^2 + \dots .$$

The q_t^J term is simpler than other $\tilde{H}_{24}$ terms of the effective Hamiltonian and is found to be independent of the quartic potential constants and to depend only linearly on the cubic potential constants. A theoretical formula for q_t^J is obtained and compared with experimental measurements. The high-J limiting behavior of the energy levels with $V_t > 1$ is also discussed.

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RE4. (2:21)

HIGHER-ORDER VIBRATION-ROTATION CONSTANTS OF THE X_3 MOLECULE

JAMES K. G. WATSON

Higher-order vibration-rotation perturbation calculations are unusually simple for the equilateral triangular X_3 molecule because the main Coriolis terms H_{21} are diagonal in a harmonic representation, so that the corresponding contact transformation function S_{21} vanishes. Formulas are obtained for several higher-order molecular parameters, including the vibrational dependence of the centrifugal and Coriolis constants. The attempted application of these formulas to data for H_3^+ and D_3^+ will be discussed.

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RE5. (2:38)

SIMULATED ELECTRONIC SPECTRA OF HCN AND CNH OBTAINED WITH THE SEMIRIGID BENDER MODEL

S. C. ROSS AND P. R. BUNKER

The Semirigid Bender (SRB) model has been used to study the complete internal rotation of HCN into CNH for both the ground and first excited electronic states. The bending potential functions of these two states were obtained by fitting the SRB model to experimentally observed vibrational energies and by incorporating various *ab initio* results where experimental data was lacking. The SRB wavefunctions obtained from these potential functions, combined with wavefunctions for the stretching vibrations, were then used to simulate the electronic spectra for both HCN and CNH.

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RE6. (2:50)

SENSITIVITY OF QUASI-EQUILIBRIUM SEMIRIGID MODELS TO ISOTOPIC SUBSTITUTION

G. A. NATANSON

As shown by the author[1] the maximum separation between a large-amplitude internal motion and small-amplitude vibrations can be reached by the use of so-called quasi-equilibrium semirigid models uniquely determined by the gradient of the adiabatic potential.

In contrast with semirigid bender models suggested by Bunker and Landsberg[2] quasi-equilibrium models depend on nuclear masses; and as a result asymmetric isotopic substitution breaks their point symmetry. The role of such symmetry breaking is analyzed for deutero-derivatives of water and ammonia molecules. Vibrational energy levels calculated for different cuts of the 3-dimensional potential function are compared with the accurate calculations carried out by Carney et al[3] for various isotopes of water.

1 G.A.Natanson, Molec. Phys., 46, 481, 1982.
2 P.R.Bunker, B.M.Landsberg, J. Molec. Spectrosc., 67, 374, 1977.
3 G.D.Carney, L.A.Curtiss, and S.R.Langhoff, Appl. Spectrosc., 30, 453, 1976.

Address: Department of Chemistry, The University of Chicago, 5735 Ellis Ave., Chicago, Ill. 60637.

RE7. (3:15)

THE NONRIGID BENDER HAMILTONIAN FOR A QUASILINEAR TRIATOMIC MOLECULE AND ITS APPLICATION TO CH_2

PER JENSEN AND P.R. BUNKER

The nonrigid bender Hamiltonian for the triatomic molecule was developed by Hoy and Bunker[1] and used by these authors to fit experimental data for the bent H_2O molecule. In the course of using this Hamiltonian to calculate the rotation-vibration energy levels of CH_2[2,3] it was found that for a quasilinear or linear molecule it is necessary to include some previously neglected terms and to group some of the terms in a special way before attempting to calculate the eigenvalues. These modifications will be discussed.

The 61 available experimental transition frequencies for the three methylene isotopes $^{12}CH_2$, $^{13}CH_2$ and $^{12}CD_2$ in the $\tilde{X}^3B_1$ ground state have been simultaneously fitted using the nonrigid bender model, a refined potential surface for this electronic state being obtained. The results of the fit will be presented together with predictions of the stretching frequencies, which have not been observed experimentally.

---

[1] A.R. Hoy and P.R. Bunker, J. Mol. Spectrosc. 52, 439 (1974); ibid. 74, 1 (1979).

[2] Per Jensen, P.R. Bunker and A.R. Hoy, J. Chem. Phys. 77, 5370 (1982).

[3] P.R. Bunker and Per Jensen, J. Chem. Phys., to be published.

Address: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6.

RE8. (3:32)

HCNO AS A SEMIRIGID BENDER: THE DEGENERATE ν_4 STATE

B. P. WINNEWISSER AND PER JENSEN

The manifold of large amplitude states (due to the HCN bending vibration at 224 cm^{-1}) superimposed on the ν_4 CNO bending state at 537 cm^{-1} for fulminic acid HCNO has been analyzed using a modified version of the semirigid bender model previously described by Bunker et al.[1] The ν_4 bending mode is degenerate in the linear limit and the semirigid bender Hamiltonian has been modified to account for the ν_4 vibrational angular momentum around the molecular axis in the linear limit, and for ℓ-doubling effects.

Some of the experimental data used in this analysis were obtained from a spectrum of HCNO between 500 and 660 cm^{-1} recorded on the high-resolution infrared Bomem interferometer at the Herzberg Institute of Astrophysics, Ottawa. From this spectrum, molecular constants have been determined for a number of vibrational states not previously observed: $\nu_4^{\pm 1} + 2\nu_5^{0}$, $\nu_4^{\pm 1} + 3\nu_5^{\,1\mp}$ and $\nu_4^{\pm 1} + 3\nu_5^{\pm 1}$.

---

[1] P.R. Bunker, B.M. Landsberg and B.P. Winnewisser, J. Mol. Spectrosc. 74, 9 (1979).

Address of Winnewisser: Physikalisch-Chemisches Institut, Justus-Liebig-Universitaet Giessen, D-6300 Giessen, West Germany.
Address of Jensen: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6.

RE9. (3:44)

CALCULATION AND INTERPRETATION OF THE VIBRATIONAL SPECTRA OF INTERACTING MOLECULES

STEVEN CHIN, T.A. FORD AND WILLIS B. PERSON

A system of programs has been developed to predict and interpret the infrared spectra of molecules and different chemically interacting species of interest. The frequency parameters (or force constants) and the intensity parameters (or Atomic Polar Tensors (APT) are calculated using the Gaussian 76 program for *ab initio* quantum mechanical calculations with a 4-31G basis set. The resultant frequencies and intensities have been used to predict the fundamental infrared spectrum of water molecules interacting with different molecular and ionic species. The corresponding frequency shifts and intensity changes from the spectrum of the non-interacting water molecule are dependent upon both the geometrical orientation and the electron-donating properties of the interacting species. The intensity parameters can be further analyzed by using the charge, charge-flux, overlap (CCFO) interpretation of the APT. This interpretation is helpful to pin-point the exact source of the perturbation that produces the intensity change. The significance will be discussed of each of these CCFO terms in predicting infrared intensities of molecules undergoing intermolecular interaction.

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RE10. (4:01)

ON THE COLLISION DYNAMICAL ORIGINS OF PRESSURE BROADENING

J. GELFAND, J. J. BELBRUNO, K. VERGES, AND H. RABITZ

We have used the energy corrected sudden scaling theory approach to extract the component collisional interactions of pressure broadened linewidths. Utilizing this approach we have been able to account for the linewidths and their trends in the fundamental and overtone bands in the HF, DF, HCl and CO systems, both self broadened and with various collision partners.[1,2,3] The results of these studies have allowed us to understand the behavior of pressure broadening in terms of the underlying collision dynamics. We have found for example in the HF and HCl systems that rotation-rotation energy transfer collisions are the greatest contributors to the linewidths. Furthermore trends in the linewidths are dominated by the energetics of these types of collisions. On the other hand, rotation-translation energy transfer collisions produce the dominant contributions to the self broadened linewidths of CO and energetics are not as important a consideration. In all systems studied so far we find that contributions due to elastic collisions are small except for reorientation collisions for transitions arising from low J states. The effect of collision partners in the CO system will be reported. The temperature dependence of pressure broadening will be discussed in terms of the underlying collision dynamics.

[1] DePristo et al, J.C.P. 74, 5031 (1981).

[2] BelBruno et al, J.C.P. 75, 4927 (1981).

[3] BelBruno et al, J.C.P., Flygare Memorial Issue, in press (March 1983).

Address of Gelfand and Verges: Applied Physics & Materials Laboratory, Department of Mechanical & Aerospace Engineering, Princeton University, Princeton, New Jersey, 08544.
Address of BelBruno: Department of Chemistry, Dartmouth College, Hanover, New Hampshire, 03755.
Address of Rabitz: Department of Chemistry, Princeton University, Princeton, New Jersey, 08544.

RE11. (4:18)

NITROGEN BROADENED HALFWIDTHS OF HF IN THE 1-0 BAND

R. E. THOMPSON, J. H. PARK, M. A. H. SMITH, G. A. HARVEY, AND J. M. RUSSELL, III

Nitrogen-broadened halfwidths for seven lines in the fundamental infrared band of HF have been determined from laboratory measurements at room temperature. The spectra were recorded using a Fourier-transform spectrometer with a nominal resolution of 0.060 cm^{-1}. A non-linear least squares spectral fitting technique was used in the data analysis to obtain halfwidth values for the P3 through R3 lines with an average uncertainty of approximately 15%.

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RE12. (4:30)

VIBRATIONAL SPECTRA FROM SEMI-CLASSICAL MECHANICS

D. M. WARDLAW, D. W. NOID, AND R. A. MARCUS

A spectral analysis method for classical trajectories, presented in Ref. 1, has been used fairly extensively to examine the dynamical properties of molecular and model systems. Results with this technique were shown to be in excellent agreement with quantum mechanical results for the vibrational transition frequencies and dipole matrix elements of a Morse oscillator.[2] In the present lecture, transition intensities for non-resonant and resonant Hamiltonian systems are discussed. Current work is aimed at applying the technique to the vibrational degrees of freedom of triatomic molecules. Advantages and limitations of this spectral analysis are considered.

[1] D. W. Noid, M. L. Koszykowski and R. A. Marcus, J. Chem. Phys. 67, 404 (1977).
[2] M. L. Koszykowski, D. W. Noid and R. A. Marcus, J. Chem. Phys. 86, 2113 (1982).

Address of Wardlaw and Marcus: Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California, 91125.
Address of Noid: Oak Ridge National Laboratory, Oak Ridge, Tennessee, 37830.

RE13. (4:47)

ANHARMONICITY CONSTANTS IN ACETAMIDE AND THIOACETAMIDE

SIBSANKAR BALA, PRABHAT K. PANJA AND PRADIP N. GHOSH

The vibrational spectra of acetamide and thioacetamide have been recorded. The 1300-1400 cm^{-1} regions of both the compounds exhibit Fermi resonances. The equations for Fermi polyad have been set up to obtain a number of anharmonic coupling constants from the observed frequencies and their intensity ratios. These constants have been used to obtain a set of anharmonicity constants. The IR spectrum of acetamide exhibits a few hot bands tentatively arising from intermolecular hydrogen bonding N-H...O. A potential function is presented for this bond which can yield the intermolecular force constant.

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RE14. (4:57)

VIBRATIONAL SPECTRUM AND NEARLY FREE INTERNAL ROTATION

SAJAL K. GANGULY AND PRADIP N. GHOSH

The effect of coupling of a large amplitude internal rotation with the other 3N-7 normal modes of vibration of an asymmetric molecule containing a symmetric internal rotor has been evaluated. The perturbation due to internal rotation has been expressed in terms of torsional coriolis coupling and similar terms contining the torsional angle derivative of the normal modes. By retaining only the lower order terms in these coupling constants the first and second order correction due to perturbation are evaluated with an unperturbed basis as the product harmonic oscillator wavefunctions of the 3N-7 normal modes and the free internal rotation wavefunction.

Numerical calculations are carried out for trans methyl nitrite which has has a very low barrier to internal rotation. The variation of normal coordinates with the torsional angle has been calculated by direct numerical computation. The torsional coriolis coupling leads to a significant shift of the normal modes of vibration. The variation of normal modes with the torsional angle shows a small contribution.

The effect of vibration-internal rotation interactions on the hot band frequencies due to internal rotation are also evaluated. The small contributions show that the kinetic energy effect on the hot band spacing is small and should be expressed in terms of potential energy coupling(1).

---

[1] S.K.Ganguly and P.N.Ghosh,Chem. Phys. Letters, 90,140,1982.

Address of Ganguly and Ghosh : Department of Physics, University of Calcutta, 92, A.P.C. Road, Calcutta-700009, India.

RF1. (1:30)

HIGH RESOLUTION PHOTOELECTRON SPECTRUM OF THE $\tilde{B}$ ($^2\Pi_i$) STATE OF N_2O^+

T. CVITAŠ, L. KLASINC, B. KOVAČ, AND R. MCDIARMID

The long, irregular vibrational structure of the $\tilde{B}$ ($^2\Pi_i$) state of N_2O^+ is interpreted as a progression of Fermi resonances between pairs of vibrational subbands of the $\tilde{B}$ state that correspond to $2\nu_2 + (v-1)\nu_1$ and $v\nu_1$. Because of anharmonicity in the ν_1 progression, the separations between successive pairs of interacting bands vary throughout the progression, resulting in variable magnitude Fermi interactions. This model, rather than the more usual one that incorporates overtones of ν_2, is shown to accurately describe the experimental data.

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RF2. (1:42)

INVESTIGATION OF THE 550 nm REGION OF SUPERSONICALLY COOLED NO_2

MENG-CHIH SU and DAVID L. MONTS

The visible system of nitrogen dioxide is notoriously complex.[1] Low resolution absorption spectra clearly shows a sudden increase in intensity and in complexity beginning at about 550 nm. We report our investigation of the 550 nm region of NO_2 cooled in a supersonic expansion, and we discuss the relationship of this change to the electronic states of the molecule.

---

[1] D.K. Hsu, D.L. Monts, and R.N. Zare, Spectral Atlas of Nitrogen Dioxide (Academic Press, New York, 1978).

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RF3. (1:59)

SPIN PERTURBATIONS IN THE NO_2 VISIBLE SYSTEM

DAVID L. MONTS and MENG-CHIH SU

Rotational analysis of the nitrogen dioxide visible system has revealed extensive spin perturbations. An example of the complexity of the spin perturbations is provided by the $K_a' = 0$ subband of the 612.5 nm band: the lower energy spin components are strongly perturbed while the higher energy spin components are relatively unperturbed although the two spin states are expected to have identical symmetry ($E_{1/2}$). Possible perturbation mechanisms are discussed and the perturbation is compared to that of ClO_2 which also exhibits a spin state-dependent perturbation.[2]

---

[1] D.L. Monts, B. Soep, and R.N. Zare, J. Mol. Spectrosc, 77, 402-428 (1979).
[2] S. Michielsen, A.J. Merer, S.A. Rice, F.A. Novak, K.F. Freed, and Y. Hamada, J. Chem. Phys. 74, 3089-3101 (1981).

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RF4. (2:16)

Collisional Transfer of Rotational Energy in the $^2B_1$ Electronic State of Nitrogen Dioxide and Improved Vibrational and Rotational Constants for the (0,2,0) and (0,3,0) States

J.L. Hardwick

Collisional satellite lines have been observed in fluorescence from nitrogen dioxide excited by the 4545Å line of the argon laser. The $13_{0,13}$ level of the (0,8,0) vibrational level of the $^2B_1$ electronic state is populated by the laser and undergoes collisional relaxation to the $11_{0,11}$, $15_{0,15}$, and $17_{0,17}$ rotational levels of the same vibronic state. These collisionally populated states are identified by their fluorescence to well-known levels of the ground electronic state and by comparison with the absorption spectrum. Collisional satellites are also observed for fluorescence to the (0,2,0)" and (0,3,0)" states. These transitions, together with unrelaxed fluorescence lines, are used to obtain improved band origins and rotational constants for those vibrational states.

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RF5. (2:33)

THE NEAR ULTRAVIOLET ABSORPTION SPECTRUM (Σ BANDS) OF $^{12}C^{34}S_2$

J. L. HARDWICK, C. J. SELISKAR, AND C. KINARD

The absorption spectrum of $^{12}C^{34}S_2$ carbon disulfide has been photographed at high resolution in the region 25500 to 29200 cm^{-1}. Several hot bands with $K=\ell=0$ have been analyzed in the $\tilde{a}^3A_2$-$\tilde{X}^1\Sigma_g^+$ system (Kleman R system) and ground state B values and vibrational constants have been determined for $v_2'' = 2$ and 4. Excited $\tilde{a}^3A_2$ state B values and vibrational constants have been determined for $v_2' = 3, 4, 5$ and 6 and $v_1' = 0$ and 1. Further work on this band system as well as accompanying ones in the same spectral region is in progress.

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RF6. (2:50)

ROTATIONAL PERTURBATION AND ZEEMAN EFFECT IN THE $\tilde{A}^1A''-\tilde{X}^1A'$ TRANSITION OF HCF

T. SUZUKI, S. SAITO, AND E. HIROTA

Merer and Travis reported that the $\tilde{A}^1A''(010)-\tilde{X}^1A'(000)$ vibronic transition of HCF was remarkably perturbed.[1] In view of the importance of carbene derivatives in various fields, we investigated this HCF band by cw dye laser spectroscopy with the Doppler-limited resolution. Furthermore, we studied the perturbed lines of the band under the magnetic field up to 2.3 T. HCF was produced by the reaction of microwave discharged CF_4 with CH_3F.

The subbands of $K_a'-K_a'' = 3-4, 2-3, 1-2, 0-1, 1-0, 2-1, 0-0, 1-1, 2-2, 2-0,$ and 0-2 were assigned using ground state combination differences. Every subband was found to be perturbed to some degree. The perturbations observed in this band were very irregular except the low J transitions with $K_a'=1$. The perturbations for the $K_a'=1$ levels were well explained by an electronic Coriolis interaction with a highly excited vibrational level in the electronic ground state. The irregularly perturbed lines often showed considerably large magnetic activity. Therefore the origin of some of these perturbations has been believed to be the lowest triplet state.

[1]A. J. Merer and D. N. Travis, J. Mol. Spectrosc. 44, 15 (1966).

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RF7. (3:15)

LASER EXCITATION SPECTRUM AND MICROWAVE OPTICAL DOUBLE RESONANCE SPECTRUM OF THE 3_0^1 BAND IN THE $\tilde{a}^3A_2-\tilde{X}^1A_1$ SYSTEM OF H_2CS

T. SUZUKI, S. SAITO, AND E. HIROTA

The cw dye laser excitation spectrum of the 3_0^1 band in the $\tilde{a}^3A_2-\tilde{X}^1A_1$ transition of H_2CS was observed in the region 15280 to 15400 cm^{-1} with Doppler-limited resolution. H_2CS was generated by thermally decomposing $(CH_2)_3S$. The observed spectrum was analyzed to yield precise values for the rotational constants, the centrifugal distortion constants, and the spin-spin and spin-rotation interaction constants in the upper triplet state and for the band origin. Transitions with $K_a'=4$ and 5 revealed the effect of the c-type Coriolis interaction between the $v_3'=1$ and $v_6'=1$ states. Through the analysis of this Coriolis interaction the $\nu_3-\nu_6$ difference was determined to be 99.322 cm^{-1}.

Fifteen K-type doubling transitions of $K_a=1$ and 2 and two a-type R branch transitions with $K_a=1$ in the $\tilde{a}$ state were observed by a microwave or radio-frequency optical double resonance technique. Two K-type doubling transitions of $K_a=1$ and two R branch transitions were resolved into three hyperfine components. From the observed splitting the proton hyperfine constants were determined to be $a_F=27.7(25)$, $T_{bb}+T_{cc}=12.8(44)$, and $T_{bb}-T_{cc}=7.89(19)$ with one standard errors in parentheses.

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RF8. (3:32)

WHY IS FORMALDEHYDE NONPLANAR IN ITS $S_1(\pi^*,n)$ ELECTRONIC STATE?

K. K. INNES

Abnormally low energy levels observed for the out-of-plane vibration $\nu_4(b_1)$ of the $\tilde{A}^1A_2(S_1)$ electronic states of H_2CO, HDCO and D_2CO are modeled in turn by means of two-state calculations of vibronic coupling between S_1 and a higher-lying singlet state $\tilde{B}^1B_2(S_2)$. The active vibration is ν_4. In each case the vibronic calculations reproduce also the large positive anharmonicity of ν_4 in the S_1 state; the calculated vibrational spacing alternates as observed and consistent with the known pyramidal geometry. Accordingly, the known double-minimum potential for ν_4 in the S_1 electronic state is attributed to vibronic interaction of S_1 and S_2 with consequent "pseudo Jahn-Teller distortions." Vibronic coupling of S_1 and S_2 by ν_4 was earlier proposed to account for most of the intensity of the (electric-dipole-forbidden) S_1-S_0 transition. The coupling constant estimated from the intensity data is close to that obtained in the present modeling of energy levels. This agreement is taken as confirmation that the coupling is a major cause of the change of shape of formaldehyde in its S_1-S_0 transition. The more extreme distortion of the potential of the analogous triplet state $^3A_2(\pi^*,n)$ of D_2CO also is modeled successfully.

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RF9. (3:49)

THE ELECTRIC DIPOLE MOMENT OF THE $\tilde{A}\ ^1A_2$ STATE OF FORMALDEHYDE BY STARK QUANTUM BEATS

MARTIN CARRERA, P.H. VACCARO, H.-L. DAI, AND R.W. FIELD

Low-J rotational levels in the $v_4 = 2$ vibrational level of the H_2CO $\tilde{A}\ ^1A_2$ state are excited by a Nd:YAG pumped frequency-doubled dye laser. An electric field is applied in a direction perpendicular to the linear laser polarization. Quantum beats are observed between $|M|$ and $|M\pm2|$ levels originating from the same J_{K_a,K_c} asymmetry component. The electric field is varied over the interval 1 to 5kV/cm and quantum beats in the 4-40 MHz range are observed with an accuracy of $\pm$0.02MHz. The dependence of the measured Stark coefficient on J and K_a is a probe of Coriolis perturbations within the $\tilde{A}$ state and interactions between the prepared $\tilde{A}$ level and the "lumpy continuum" of the $\tilde{X}$ state.

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RF10. (4:06)

ZERO FIELD AND ZEEMAN QUANTUM BEATS IN THE ACETYLENE $\tilde{A}\ ^1A_u$ STATE

M. LOMBARDI, E. ABRAMSON, AND R.W. FIELD

The HCCH $\tilde{A}^1A_u$ state, when excited by 10ns pulsed radiation at 221nm from a Nd:YAG pumped, frequency doubled dye laser, exhibits at least one singlet-triplet quantum beat in the 0-200 Gauss interval for every rotational level of the $\tilde{A}$ $v_3 = 3$ $K = 1$ level examined. These experiments provide information concerning the density of triplet vibronic levels and their g_J-values as well as the singlet-triplet perturbation matrix elements.

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RF11. (4.23)

STIMULATED EMISSION SPECTROSCOPY OF H_2CO

H.-L. DAI, D.E. REISNER, P.H. VACCARO, C. KORPA, R.W. FIELD, AND J.L. KINSEY

A new technique, Stimulated Emission Pumping (SEP), has been used to examine the rotation-vibration structure of the $\tilde{X}\ ^1A_1$ state of formaldehyde at energies up to 10^4 cm^{-1}. A complete set of 21 X_{ij} anharmonicity constants has been determined from a,b, and c-type $\tilde{A} \rightarrow \tilde{X}$ transitions from the 4^1 level and from numerous Coriolis and Fermi perturbations. B and C rotational constants as well as dipole moments are observed for many highly excited levels of the $\tilde{X}$ state.

Coriolis perturbations are extremely numerous at high vibrational excitation and the SEP technique makes their analysis trivial. Although nonrotating vibrational levels exhibit large and systematic structural differences, at J ~ 10 and K ~ 3 Coriolis mixing minimizes these differences so that all properties become locally averaged. This has important implications about the possibility of level-specific chemistry.

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RF12. (4:40)

STIMULATED EMISSION SPECTROSCOPY OF ACETYLENE. STRUCTURE OF THE $\tilde{X}$ $\cdot_g$ STATE AT 28000 cm^{-1}

E. ABRAMSON, D. IMRE, J.L. KINSEY, AND R.W. FIELD

The 28000 cm^{-1} region of the $\tilde{X}^1\Sigma_g^+$ state of HCCH is examined by Stimulated Emission Pumping (SEP) from the v_3 = 2 and 3,$\tilde{K}$ = 1 levels of the trans-bent $\tilde{A}^1A_u$ excited state. In contrast to the situation for high overtone spectroscopy which accesses primarily C-H overtones of u-symmetry, SEP samples C-C and trans-bend levels of g-symmetry.

Among the most striking features in the SEP spectra are ~ 2 cm^{-1} wide clumps (about 1 clump per 10 cm^{-1}) each consisting of ~ 20 0.02 cm^{-1} wide lines. The clumps appear to be $K' = 1 \rightarrow K'' = 0$ sub-bands. Although no correlation has been found between the fine structure of clumps observed for consecutive J"-values, the centers of gravity for all observed clumps appear to be well described by a rotational constant B = 1.166 cm^{-1} which is surprisingly similar to the value B = 1.177 cm^{-1} for the vibrationless level.

Density of state calculations suggest that each clump corresponds to a combination of the three totally symmetric normal modes (in C_{2h} these are C-C stretch, symmetric H-C stretch, and trans-bend) and that the lines within each clump correspond to all states of A_g (Σ_g^+) symmetry.

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RF13. (4:57)

LASER INDUCED FLUORESCENCE SPECTROSCOPY OF MOLECULAR IONS AND IONIC CLUSTERS

TERRY A. MILLER, L. DI MAURO, M. HEAVEN, AND V. E. BONDYBEY

An excimer laser (ArF) has been used to produce 2-photon photoionization of organic molecules, e.g. C_6F_6, $C_6H_3F_3$, etc. in a free jet expansion. Laser induced fluorescence spectra of these bare ions cooled to near 0^oK has been observed. Moreover, spectra of these same ions complexed with the inert gases, He, Ne, and Ar have been recorded. A description of these ion cluster spectra will be given. Differences in spectral shifts, lineshapes, etc., and their implications for bonding energies will be described. Other observations will be briefly discussed.

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RG1. (1·30)

ASYMMETRY OF THE INTERCOLLISIONAL DIP IN PRESSURE-INDUCED INFRARED SPECTRA*

J. D. KELLEY AND S. L. BRAGG

Infrared spectra in the fundamental band of molecular hydrogen, including Q and S branch quadrupole[1,2] and pressure-induced dipole[1] features, have been analyzed. The absorption dip in the pressure-induced dipole contribution to the Q branch is seen to have a definite antisymmetric component. The dip has been previously attributed[3] to anticorrelation between the dipole moments induced in successive binary collisions; this anticorrelation produces a dip symmetric about line center.

In this work the original theoretical argument[3] has been extended to include phase shifts in the molecular wave functions resulting from the collisional interaction. The appropriate dipole moment autocorrelation function has been constructed, and the resulting absorption dip "line shape", obtained from the Fourier transform of the autocorrelation function, has both a symmetric and antisymmetric component given by

$$W(\omega) = (\omega^2\tau_c{}^2 - \omega\tau_c\sin\alpha)\ (1 + \omega^2\tau_c{}^2)^{-1}$$

for $\cos\alpha \simeq 1$. In this equation ω is the frequency measured from line center, α is the single collision phase shift, and τ_c characterizes the exponential distribution of intervals between collisions.

The data for pressure-induced Q(0) and Q(1) absorption dips are shown to be well fit by $W(\omega)$, and the value obtained for α ($\sim$ 0.1 rad) is consistent with a simple repulsive interaction collision model.

*This work is supported by the McDonnell Douglas Independent Research and Development Program.

1. S. L. Bragg, "An Experimental Study of the Vibrational -Rotational Spectrum of Molecular Hydrogen", thesis, Washington University (1981).
2. S. L. Bragg, J. W. Brault, and W. H. Smith, Ap. J. 263, 999 (1982).
3. J. Van Kranendonk, Can. J. Phys. 46, 1173 (1968).

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RG2. (1.47)

OBSERVATION OF THE $\Delta J = 5$ PURE ROTATIONAL TRANSITION IN SOLID HD

CHEN-HSIN LIEN, K. K. LO, J. R. GAINES, and K. NARAHARI RAO

The infrared spectrum of solid HD has been obtained using a Fourier Transform Spectrometer with a resolution of 0.04 cm^{-1}. The $\Delta J = 5$ transitions in the pure rotational and vibration-rotation regions have been observed. The measured wavenumbers are 1318.26 cm^{-1} for the $V_0(0)$ and 4486.66 cm^{-1} for the $V_{1\leftarrow 0}(0)$ transitions. An attempt to interpret this transition by 32-polar induced dipole moment yields a theoretical value of the integrated absorption coefficient $\tilde{\alpha}$ as 1.4×10^{-16} cm^{3}s^{-1}. This compares well with the measured integrated absorption coefficient 1.1×10^{-16} cm^{3}s^{-1} for $V_0(0)$.

The $U_0(0)$ and $V_{1\leftarrow 0}(0)$ transitions have also been observed and their integrated absorption coefficients have been measured. The $\Delta J = 3$ transitions are found to be overlapped by the double transitions of HD. However, the $T_{1\leftarrow 0}(0)$, $Q_{1\leftarrow 0}(0) + T_0(0)$ transitions have been identified.

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RG3. (2:04)

HIGH RESOLUTION SPECTROSCOPY OF THE OVERTONE BANDS OF HD*

B. A. HARE, M. E. MICKELSON+, AND J. T. TRAUGER+

High resolution spectra of the 2-0 through 6-0 vibrational-rotational bands of the hydrogen deuteride molecule have been obtained using the Kitt Peak Solar FTS at a resolving power in excess of 600,000. Measurements were made on a room temperature gas sample contained in a 2-meter White cell. Pressures ranging from 200 to 1400 torr were used at a pathlength of 56 meters. Line positions, pressure shifts, intensities, and line profiles have been determined. A value for the self-broadening pressure-broadening coefficient has been determined from nonlinear least-squares fits to a Galatry model. Additionally, a set of equilibrium constants will be presented based on these and other precision line positions.

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+Visiting Astronomers, Kitt Peak National Observatory, operated by AURA Inc., under contract with NSF.

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RG4. (2:16)

RAMAN SPECTROSCOPY OF HYDROGEN ISOTOPES: DETERMINATION OF EFFECTS OF CHANGES IN POLARIZABILITY ANISOTROPY ON INTENSITIES

KIRK VEIRS and GERD M. ROSENBLATT

Accurate rotational-vibrational relative intensities of each of the isotopic species of hydrogen are determined from gas phase Raman spectroscopy. Previously unreported line positions for D_2, HT, DT, and T_2 have been determined. The Raman shifts agree with theoretical energy levels for D_2 (theoretical values for Tritium containing species are not available), but differ from published spectroscopic constants at high J. The results have implications for the application of Raman-based spectroscopies of hydrogen as a temperature or state-population probe in high temperature systems.

An external cavity configuration for an Ar^+ laser was constructed which delivers 160 Watts at 488 nm for gas phase Raman spectroscopy. A Spex 1403 double monochromator with photon counting and digital data collection allows accurate intensity measurements to be made. O- and S-branch rotational-vibrational line intensities are measured for H_2, D_2, T_2, HD, HT, and DT with an order of magnitude increase in precision and accuracy over earlier measurements on H_2 and D_2.

The first derivative of the polarizability anisotropy with respect to internuclear distance may be extracted using first-order perturbation theory (it is expected, however, that first-order perturbation theory is inadequate to describe the rotational-vibrational Raman intensities of hydrogen isotopes). Neglecting the variation in polarizability anisotropy can lead to 10% errors in the determined temperatures or state-populations when using Raman spectroscopy of hydrogen as a probe in high temperature systems (above 1000K).

Line positions up to the pure rotational S(8) transition in D_2 and the Q(11) transition in T_2 were seen and the predicted positions using the most recent molecular constants were in error by 1.5 cm^{-1}. For high J values the line positions are best determined from theoretical calculations as the molecular constants cannot be accurately extrapolated beyond the highest J values (above J=6 in H_2) used in their determination.

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RG5. (2.28)

RAMAN SPECTRUM OF PYRIDINE RESONANT TO THE $S_2(\pi-\pi^*)$ STATE*

I. SUZUKA, Y. C. CHUNG AND G. E. LEROI

The Raman spectrum of pyridine (C_5H_5N), resonant to the $S_2(\pi-\pi^*)$ excited electronic state, has been studied in the vapor phase under 266.0 nm excitation. The active vibrational modes and the scattered intensity distribution are very different from those of the preresonance Raman spectrum of the $S_1(n-\pi^*)$ state.[1] The observations will be compared to previous studies on benzene[2] and pyrazine,[3] and interpreted in terms of vibronic coupling.

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[1] Y. Mochizuki, K. Kaya and M. Ito, J. Chem. Phys. 65, 4163 (1976); Chem. Phys. 54, 375 (1981).

[2] L. D. Ziegler and co-workers, J. Chem. Phys. 67, 2753 (1977); 68, 1248 (1978); 74, 15 (1981).

[3] I. Suzuka, Y. Udagawa and M. Ito, Chem. Phys. Letters 64, 333 (1979).

*Research supported in part by the U. S. National Science Foundation

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RG6. (2:45)

PRERESONANCE RAMAN EXCITATION PROFILES OF CAROTENOIDS*

C. M. PHILLIPS AND G. E. LEROI

It is now well established[1] that the lowest excited singlet electronic state in linear polyenes of at least moderate length has the same parity as the ground state, and is thus forbidden in normal one-photon absorption. The (allowed) $1^1B_u \leftarrow 1^1A_g$ transition energy reaches an asymptotic value for long polyene chains; however, the corresponding behavior for the $2^1A_g \leftarrow 1^1A_g$ excitation has not been determined. In order to locate this "hidden" state in polyenes possessing 9-15 C=C bonds, we are studying the preresonant Raman scattering from a series of carotenoids. The relative intensity of the C=C stretch of the solute to a neighboring cyclohexane solvent mode is measured as the exciting line is tuned through the region of interest. The presence of an underlying state is manifest by interference features on the Raman excitation profile,[2] and we have interpreted the profile of β-carotene (n=9) accordingly.[3] We report here corresponding measurements for lycopene (n=11) and decapreno-β-carotene (n=13). Estimates of the 2^1A_g state origin based on these observations will be presented, and trends in the energy gaps with variation in chain length will be discussed.

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*Research supported in part by the U. S. National Science Foundation.

[1] B. S. Hudson, B. E. Kohler and K. Schulten, in *Excited States, Vol. 6*, E. C. Lim, ed (Academic Press, New York, 1982).

[2] J. Friedman and R. M. Hochstrasser, Chem. Phys. Letters 32, 414 (1975).

[3] R. J. Thrash, H. L.-B. Fang and G. E. Leroi, J. Chem. Phys. 67, 5930 (1977).

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RG7. (3:15)

AQUEOUS PYRIDINE BOROHYDRIDE-SILVER SOLS. I. DEPOLARIZATION RATIOS AND POLARIZATION DISPERSION

Howard D. Stidham and Scott M. Harris

Depolarization ratios of surface enhanced Raman scattering (SERS) active fundamentals of pyridine in aqueous sodium borohydride generated silver sols are reported for a number of different pyridine concentrations. Observed depolarization ratios fluctuate substantially in intervals of time short compared with the time required to complete depolarization ratio measurements. These ratios are between 1 and 1/3, are essentially the same for all SERS active pyridine vibrations in a particular preparation, and evolve in time toward a limiting value of 1/3. Dispersion of polarization which evolves in time is found in the so-called molecule-metal stretching vibration found near 225 cm^{-1}. A simple physical model of the scattering process is suggested which accords closely enough with these facts to be useful while retaining sufficient simplicity to allow qualitative insight into the behavior of these complex colloidal systems.

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RG8. (3:27)

AQUEOUS PYRIDINE BOROHYDRIDE-SILVER SOLS. II. MULTIPLE SITE ADSORPTION

Howard D. Stidham and Scott M. Harris

Raman spectra of pyridine-2,6-d_2, pyridine-3,5-d_2, pyridine-4-d and pyridine in aqueous sodium borohydride generated silver sols display time evolving multiplicity of A_1 surface enhanced Raman scattering (SERS) active bands. Addition of gelatine, polyvinyl alcohol or agar agar alters the intensity characteristics of some components of each SERS active vibration, allowing identification of bands in pyridine adsorbed onto different crystal faces of the metallic silver substrate. The isotopic data allow investigation of alterations of the molecular force field induced by adsorption onto different sites.

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RG9. (3:39)

AQUEOUS PYRIDINE BOROHYDRIDE-SILVER SOLS. III. PYRAZINE AND PYRAZINE-d

Howard D. Stidham and Andrea M. Femino

Pyrazine-d, a crystalline solid at room temperature with a melting point near 55°C, has been prepared. The Raman spectrum of the melt well above the melting point and the infrared spectrum of the vapor are presented. The molecular symmetry is reduced by the isotopic substitution to C_s, and the vibrations are all either in-plane or out-of-plane. Those with C type contours in the infrared must have depolarized Raman counterparts, and those with polarized Raman bands must have infrared counterparts that lack the strong central prominence of the typical type C band. Preliminary assignments are given and compared with results of earlier investigations of isotopic pyrazines. The state of polarization of Raman bands of pyrazine and pyrazine-d adsorbed onto aqueous sodium borohydride generated silver sols is discussed.

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RG10. (3:51)

INTENSITY SUM RULE FOR ITERATED VIRGULATE STRUCTURES

Howard D. Stidham

Schaufele and Shimanouchi[1] first showed that the low frequency Raman active vibrations of long chain hydrocarbons could be explained as longitudinal acoustic modes associated with odd numbers of nodes, or zeroes of the motion, along the hydrocarbon chain. The experimental Raman data display intensities that are qualitatively described in the original work, in which a polarization dependence of the form

$$\alpha = \alpha_o + \alpha_1 \Sigma_i \Delta \ell_i + \ldots \qquad (1)$$

was assumed. To the extent that this bond polarizability model can be applied to real molecules, there is a precise intensity sum rule which is embedded in the mathematics of the transformation from the basis coordinates $\Delta \ell_i$ to the normal coordinates Q_m appropriate to such iterated virgulate structures. If μ is the reduced mass for the motion $\Delta \ell_i$, the sum rule has the form

$$\frac{1}{2\,\mu\,\alpha_1{}^2} \sum_{m_{odd}=1}^{n-1 \text{ or } n-2} (\partial\alpha/\partial Q_m)^2 = 1 \qquad (2)$$

In this paper, this intensity sum rule will be derived, and the scope of applicability will be discussed. Some real physical examples will be presented.

[1] R. F. Schaufele and T. Shimanouchi, J. Chem. Phys. 47, 3605 (1967).

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RG11. (4:03)

TIME RESOLVED RESONANCE RAMAN SPECTROSCOPY OF PHENOXYL RADICALS

G.N.R. TRIPATHI AND R.H. SCHULER

Time resolved resonance enhanced Raman spectra of a number of phenoxyl radicals, produced in the pulse radiolytic oxidation of aqueous solutions of phenols, have been obtained and analysed. These radicals absorb in the spectral region 390-450 nm ($\varepsilon \sim 3\text{-}7\times10^3\ M^{-1}cm^{-1}$) and exhibit moderate but sufficient resonance enhancement when excited at their absorption peaks to be detected at microsecond times at $\sim 10^{-5}$ M concentrations. They are highly reactive and have been observed to decay at diffusion controlled rates ($k > 10^9\ M^{-1}s^{-1}$). The observed resonance Raman spectra, their structural implications and decay kinetics will be discussed.

Address - Radiation Laboratory and Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556

RG12. (4:20)

CARS MEASUREMENTS IN TURBULENT FLAMES

L. P. GOSS

A CARS system capable of simultaneous thermometry and N_2-number-density measurements has been designed, constructed, and used to study a very turbulent propane diffusion flame. The CARS data obtained with this instrument were used to construct probability density functions, correlation diagrams, and contour maps of the turbulent flame. A comparison of the measured flame quantities with adiabatic flame predictions will be discussed.

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RG13. (4:37)

ULTRASENSITIVE COHERENT RAMAN SPECTROSCOPY OF THIN FILMS AND SURFACES

W. M. HETHERINGTON, G. I. STEGEMAN, R. M. FORTENBERRY AND N. E. VAN WYCK

The structures of thin films, surfaces, and adsorbed surface species can be investigated using a new nonlinear optical method based on coherent Raman scattering and planar optical waveguides. Vibrational spectra are obtained from species in or on thin films into which laser beams have been coupled. Surface species down to submonolayer coverages can be detected through a coherent Raman interaction with the evanescent fields extending above the film. Extensive calculations have been performed, including background reduction considerations, which agree with the experimental results based on polymer and metal oxide films.

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Address of Stegeman and Fortenberry: Optical Sciences Center, University of Arizona, Tucson, Arizona, 85721

RG14. (4:52)

TRANSIENT GRATING SPECTROSCOPY USING THE PHASE CONJUGATE CONFIGURATION

E. J. HEILWEIL and R. M. HOCHSTRASSER

The picosecond time dependence of a specific nonlinear signal generated in the fully resonant and degenerate phase conjugate configuration is presented. This particular Fourier component was explored in a previous nonlinear optical mixing experiment (H. Souma, E.J. Heilweil, R.M. Hochstrasser, J. Chem. Phys. 76(12),5693, 1982) where it was found to contain both electronic and thermal relaxation contributions. These portions are clearly time resolved in the present study where features arising from optical mixing and subsequent thermal grating formation and decay are exhibited.

Experiments performed on the dyes Rhodamine 6G and Cresyl Violet in ethanol as well as aqueous colloidal gold solutions will be discussed. Nonradiative energy deposition of heat into the solvent by excited state vibrational energy relaxation and thermal conduction from transiently cooling metal spheres is demonstrated by these systems.

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RH1. (1:30)

INFRARED SPECTRA OF MATRIX ISOLATED HYDROGEN FLUORIDE AND VIBRATIONAL PREDISSOCIATION OF THE DIMER, R. L. REDINGTON AND D. F. HAMILL

Infrared spectra are reported for HF species and their deuterated isotopomers isolated in solid Ar, N_2, and CO and in various binary mixed matrices. HF stretching and FH···F bending fundamentals are observed for several dimer isotopomers. The HF molecule forms appreciable hydrogen bonds with CO and H_2O, and HF stretching frequencies are reported for the Ar-isolated bimolecules FH···X, with X = Kr, Xe, N_2, CO, and H_2O. The Ar matrix isolation data are compared with the vapor phase infrared absorption data and the laser-induced vibrational predissociation data, and values are proposed for all six fundamental frequencies of the dimer. In an attempt to reconcile the various observations, our analysis also includes a predissociation lifetime correlation suggested to us by current theory. It makes use of the vibrational predissociation lifetime ranges reported for bands in the HF stretching region. The proposed interpretation suggests a low picosecond timescale for vibrational predissociation of the ν_2 state, with longer lifetimes associated with proposed ν_1 and $\nu_2 + \nu_5$ states. The observed lifetime ranges correlate with the relative translational energies of the product monomers when it is assumed that the excitation energy quickly accesses similar incipient vibrational predissociation channels from any of the initially excited vibrations.

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RH2. (1:47)

MATRIX ISOLATION STUDY OF SO_2·AMINE COMPLEXES

Craig S. Sass and Bruce S. Ault

The infrared spectra of the reaction products of SO_2 with NH_3, CH_3NH_2, $(CH_3)_2NH$ and $(CH_3)_3N$ were studied in both argon and nitrogen matrices. The 1:1 adducts of SO_2 with all of the bases were observed, as was the 1:2 adduct of SO_2 with NH_3. It was found that the frequency of the S-O stretching modes decreased with increasing basicity of the amine. For example, ν_3 decreased from 1338 cm^{-1} in $SO_2 \cdot NH_3$ to 1270 cm^{-1} in $SO_2 \cdot N(CH_3)_3$. This indicates that SO_2 acts as a π^* acceptor. A correlation can then be made between the force constants of the complexed SO_2 and the proton affinity of the base.

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RH3. (2:04)

INFRARED MATRIX ISOLATION STUDIES OF REACTIVE OXYANIONS

Shelle J. David and Bruce S. Ault

The oxide salt/molecule reaction technique was recently developed for the formation of oxyanions in matrices, through the transfer of O^{2-} from Tl_2O to a suitable acceptor. The reaction of Tl_2O with Ar/SO_2 produced a number of product bands. Moreover, the concentration and temperature dependence of the product bands suggested that more than one species was formed. The first set of bands has been assigned to the SO_3^{2-} anion with an effective symmetry of less than C_{3v} due to ion pairing. The second series of product bands has been assigned to the symmetrical $O_2SOSO_2^{2-}$ structure for the disulfite ion. This technique is currently being applied to the reaction of Tl_2O with BF_3 in inert matrices. To date, no assignments have been made for the product species.

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RH4. (2:21)

MATRIX ISOLATION VIBRATIONAL SPECTRA OF METAL COORDINATED OXYANIONS. THE USE OF ISOTOPE PATTERNS AND BAND INTENSITIES IN STRUCTURAL CHARACTERIZATION OF HIGH TEMPERATURE MOLECULES

L. BENCIVENNI, K.A. GINGERICH AND H.M. NAGARATHNA

IR and Raman spectra of alkali MXO_4 (X= Re,Ru,Cl), M_2XO_4 (X = S,Cr,Mo, W,Ru), MVO_3 and MXO_2 (X = V, Sb, As) species have been studied to establish their stucture. The metal isotopic shift of the stretching mode from high resolution IR spectra and band intensity measurements have been used to evaluate the bond angles and compared with the electron diffraction data. ^{18}O enrichment studies along with normal coordinate analyses further confirm the band assignment.

Address of L. BENCIVENNI; LABORATORIO DI SPETTROSCOPIA MOLECOLARE DEL CENTRO DI TERMODINAMICA CHIMICA ALTE TEMPERATURE (CNR), ISTITUTO DI CHIMICA FISICA, UNIVERSITÀ DI ROMA, 00185 ROMA (ITALY)

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RH5. (2:38)

INFRARED SPECTRA OF THE MATRIX-ISOLATED CHLORIDES OF IRON, COBALT, AND NICKEL

D. W. GREEN, D. P. McDERMOTT, AND A. BERGMAN

Iron, cobalt, and nickel metal cathodes were sputtered with various mixtures of $^{37}Cl_2/^{35}Cl_2/Ar$ to produce Ar matrices at 14 K that contained the mono-, di-, and trichlorides of the corresponding metal. The measured infrared absorption spectra of these matrices allowed the identification and characterization of $FeCl_2$, $FeCl_3$, CoCl, $CoCl_2$, $CoCl_3$, and $NiCl_2$. The derived vibrational constants of the electronic ground state of $^{59}Co^{35}Cl$ are $\omega_e = 457.8 \pm 3.0\ cm^{-1}$ and $\omega_e x_e = 2.0 \pm 1.5\ cm^{-1}$. The antisymmetric stretching mode frequencies of six isotopomers of $FeCl_2$, and three isotopomers of $CoCl_2$ were identified and measured. The dichlorides of iron, cobalt, and nickel were all determined, in contrast with previous work, to be nonlinear, with bond angles of 161°, 157°, and 161°, respectively. The estimated uncertainty is 5°. For both iron and cobalt trichlorides, the measured stretching mode frequencies were used to derive a Cl-M-Cl angle in excess of 120°, as would be expected for planar molecules with somewhat anharmonic vibrations. Observed adsorption peaks could be assigned to the $\nu_3(E)$ modes of planar (D_{3h}) Fe and Co trichlorides and the corresponding modes of the isotopomers. These observations strongly suggest that recent data supporting a pyramidal geometry for $FeCl_3$ should be reexamined. The geometry of $CoCl_3$ has not previously been determined.

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Address of McDermott: Department of Chemistry, Lafayette College, Easton, Pennsylvania, 18042

Address of Bergman: Department of Chemistry, Brown University, Providence, Rhode Island, 02912

RH6. (3:10)

VIBRATIONAL SPECTRUM OF THE NITROMETHYL FREE RADICAL TRAPPED IN SOLID ARGON

MARILYN E. JACOX

When F atoms produced in a microwave discharge react with nitromethane in a stream of argon carrier gas and the products are rapidly frozen at 14 K, prominent infrared absorptions of the nitromethyl free radical (CH_2NO_2) hydrogen-bonded to HF appear in the solid deposit. The application of extensive isotopic substitution studies to obtain information on the structure and the vibrational assignment of nitromethyl will be discussed.

Address: Molecular Spectroscopy Division, National Bureau of Standards, Washington, D. C. 20234.

RH7. (3:27)

LIGHT-INDUCED PREPARATION AND ISOMERIZATION OF UNSTABLE SPECIES IN LOW-TEMPERATURE MATRICES

R.P. Müller and J.Robert Huber

Using the technique of matrix-isolation (in conjunction with IR spectroscopy) we photolytically prepared a) hydrogen-bonded complexes between nitroxyl [HNO] and formaldehyde, nitroxyl and methylenemethylamine [$H_3C\text{-}N\text{=}CH_2$], b) the unstable trans-methylformate [$HCOOCH_3$] from its parent cis-species and c) the previously unknown molecule nitroso-methanol [$H_2C(OH)(NO)$] in its cis and trans conformations. With selective excitation (green and red light) the two conformers are reversibly interconvertable.

The selective, photolytic preparation of these compounds, the kinetics of this process, and the vibrational analysis are discussed.

Address: Physikalisch-Chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

RH8. (3:44)

FLUORESCENCE STUDIES OF MATRIX ISOLATED TRANSITION METAL ATOMS COMPLEXED WITH SMALL UNSATURATED MOLECULES

R. RUBINOVITZ AND E. R. NIXON

Experiments in which Fe or Co atoms are matrix isolated in argon or krypton previously doped with small amounts of ethylene, acetylene and hexafluorobutyne show a number of fluorescence bands in the yellow-red region. A study of the laser excitation frequency of these fluorescence features and our interpretation of their origins will be discussed.

Address of authors: Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, PA 19104

RH9. (4:01)

MATRIX ISOLATION STUDIES OF NUCLEIC ACID CONSTITUENTS. I. INFRARED SPECTRA OF URACIL MONOMERS

M. SZCZESNIAK, M. J. NOWAK, H. ROSTKOWSKA, K. SZCZEPANIAK, W. B. PERSON, and D. SHUGAR

Results of infrared studies of uracil and its N_1,N_3-dideuterated homologue isolated in argon and nitrogen matrices are presented and discussed in terms of normal modes predicted by quantum mechanical calculations. The effects on the spectrum of N-deuteration and of the interaction between the isolated molecule and the matrix are discussed. The quantum mechanical calculations are used to make a reasonably reliable first assignment of absorption bands to all the normal modes for the matrix-isolated uracil molecule. The wavenumbers and relative intensities for the absorption bands for the isolated molecule are related to those reported previously for uracil in the solid phase or in polar solution but differ significantly from them.

Address of all authors except Person and Shugar:

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Address of Person: Department of Chemistry, University of Florida, Gainesville, FL. 32611

Address of Shugar: Institute of Biochemistry and Biophysics, Polish Academy of Sciences, ul. Rakowiecka 36, 02-532 Warsaw

RH10. (4:18)

THEORETICAL ANALYSIS OF INFRARED ABSORPTION LINESHAPES OF HCl ISOLATED IN AN ARGON MATRIX, D.J. DIESTLER

A microscopic dynamical treatment of chemical systems comprising both light particles that require a quantal description and heavy ones that may be described adequately by classical mechanics is briefly reviewed. A (partial) classical limit of Heisenberg's equations yields a self-consistent set of "hemiquantal" equations (HQE) of motion. The adiabatic limit of the HQE, in which energy is not shared between high-frequency modes of the quantal subsystem and relatively low-frequency modes of the classical subsystem, is applied to a one-dimensional model for infrared absorption by matrix-isolated impurities. The predictions of the model are consistent with recent experimental measurements on the "Q" feature of $HC\ell$ isolated in Ar.

Address: Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

RH11. (4:35)

MATRIX ISOLATION AND FTIR SPECTROSCOPIC STUDIES OF RuO, RuO_2, RuO_3 and RuO_4

David W. Green, Jack G. Kay, Gerald T. Reedy, and George L. Zimmerman

We will report the results of matrix isolation and FTIR spectroscopic studies of ruthenium oxides obtained by sputtering natural abundance ruthenium in a hollow cathode discharge using different $Ar:{}^{16}O_2:{}^{18}O_2$ mixtures for the flow gas. The method used has been described by Green and Ervin[1] and references cited therein. Products observed in the argon matrix at 14K include RuO, RuO_2, RuO_3 and, possibly, RuO_4. Vibrational frequencies, force constants, and molecular symmetries will be reported. Comparisons will be made with published gas phase results for RuO[2] and RuO_4[3].

Calculations were made as in Ref. (1) for the various isotopomers using the FG matrix method including vibrational anharmonicity in order to estimate stretching force constants. Our interest in the lower ruthenium oxides arises from observations of RuO_4 photochemical decomposition using flash photolysis and kinetic absorption spectroscopy techniques.

This work was done at Drexel University, Bryn Mawr College, and Argonne National Laboratory. JGK and GLZ are indebted to the Division of Educational Programs, Argonne National Laboratory, for financial assistance while at Argonne.

1. D. W. Green and K. M. Ervin, J. Mol. Spectrosc. 89, 145-158 (1981).
2. R. Scullman and B. Thelin, J. Mol. Spectrosc. 56, 64-75 (1975).
3. I. W. Levin and S. Abramowitz, J. Chem. Phys. 50, 4860-4865 (1969).

Address of Green and Reedy: Chemical Technology Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439.
Address of Kay: Department of Chemistry, Drexel University, Philadelphia, Pa. 19104.
Address of Zimmerman: Department of Chemistry, Bryn Mawr College, Bryn Mawr, Pa. 19010.

FA1. (8:30)

FITTING OF VIBRATION ROTATION SPECTRA OF H_2S AND H_2Se

WM. C. LANE AND T. H. EDWARDS

Statements made at session TE of last year's symposium led us to reanalyse our data for ν_2 of H_2S and of H_2Se. For the ground state (with and without microwave data) and for the upper state we will give our results for different choices of: (a) Hamiltonian reduction, eg Watson's or Typke's (b) representation, eg prolate or oblate, and (c) highest order terms P^n included.

Address: Dept. of Physics and Astronomy, Michigan State University, East Lansing, MI, 48824

FA2. (8:47)

THE PURE ROTATION SPECTRUM OF HYDROGEN SULFIDE

C. CAMY-PEYRET, J.-M. FLAUD AND J.W.C. JOHNS

The pure rotation spectrum of hydrogen sulfide has been recorded between 50 and 300 cm^{-1} on a Fourier transform spectrometer with a resolution of 0.005 cm^{-1}. This high resolution and a good signal to noise ratio has allowed a real improvement in the precision of the wavenumbers of the rotational transitions of the three isotopic species $H_2{}^{32}S$, $H_2{}^{33}S$, and $H_2{}^{34}S$ observed in natural abundance. Lines with J as high as 22 or K_a as high as 15 have been observed for the most abundant isotope. Then for each isotope, the far infrared rotational transitions together with the available microwave data have been introduced in a least squares fit leading to the determination of precise Watson's rotational constants. Finally using these constants and a permanent dipole moment ${}^{o}\mu_x = 0.974$ D, the absorption of hydrogen sulfide in the far infrared region of the spectrum has been computed.

Address of Camy-Peyret and Flaud : *Laboratoire de Physique Moléculaire et d'Optique Atmosphérique*, CNRS, Bâtiment 221, Campus d'Orsay, 91405 Orsay Cedex, France.
Address of Johns : Herzberg Institute of Astrophysics, N.R.C., Ottawa, Ontario K 1A 0R6, Canada.

FA3. (8:59)

HIGH RESOLUTION SPECTRUM OF THE FUNDAMENTAL ν_2 OF DNCO

D. A. STEINER, K. WISHAH, S. R. POLO, AND T. K. McCUBBIN, JR.

The infrared spectrum of DNCO has been observed between 2066 cm^{-1} and 2278 cm^{-1} under high resolution. The primary feature in this region is the transition from the ground state to the fundamental vibrational level ν_2.

A strong interaction is observed for the K=1 levels of ν_2. Some combination bands are also observed in this region.

Address of Steiner and Polo: Department of Physics, 104 Davey Laboratory, The Pennsylvania State University, University Park, PA 16802

Address of Wishah: Department of Physics, University of Jordan, Faculty of Science, Amman, Jordan

Address of McCubbin: (on sabbatical) Laboratoire de Spectronomie Moléculaire, Université Pierre et Marie Curie, 4 Place Jussieu, 75005 Paris, France

FA4. (9:11)

ANALYSIS OF THE ν_2, ν_5 AND $\nu_3+\nu_6$ BANDS OF CHF_3 IN THE 8-9 MICRON REGION

G. GRANER and G. GUELACHVILI

The Fourier Transform infrared spectrum of CHF_3 has been obtained between 1000 and 2000 cm^{-1} with a resolution of 0.005 cm^{-1}. In the region 1110-1250 cm^{-1}, three bands are to be considered, namely ν_2 at 1141 cm^{-1}, ν_5 at 1158 and $\nu_3 + \nu_6$ at 1208 cm^{-1}. The two former are interacting through an X-Y type Coriolis resonance. The last one is affected by a very strong $\ell(2,2)$ resonance, as it was the case in ν_6. Moreover ν_5 and $\nu_3 + \nu_6$ are linked by a Fermi interaction. We shall explain how it was possible to assign transitions among this extremely dense spectrum of about 6000 lines. Preliminary molecular constants will also be given.

Address : Laboratoire d'Infrarouge, Université de Paris-Sud, Bâtiment 350, 91405 Orsay Cédex, France.

FA5. (9:28)

THE DIODE LASER HETERODYNE SPECTRUM OF CDF_3

JOSEPH P. SATTLER, RICHARD P. LEAVITT, AND TERRANCE L. WORCHESKY

The IR spectrum of the ν_5 band of CDF_3 has been obtained by using a diode laser heterodyne spectrometer. Hundreds of lines in the neighborhood of the 10R(J) CO_2 laser lines have been measured to within 6 MHz accuracy. The interesting feature of K = 3 splitting is observable in the $^PQ(J,3)$ branch. This IR heterodyne data complements the ν_5 rotational data of Ref. 1 and the laser Stark data of Ref. 2.

[1]M. S. Tobin, R. P. Leavitt, T. W. Daley, and W. G. Trueheart, contributed paper, this conference.

[2]E. Ibisch and U. Andresen, Z. Naturforch 35a, 1020-1029 (1981).

Address of Sattler, Leavitt, and Worchesky: U. S. Army Electronics Research and Development Command, Harry Diamond Laboratories, 2800 Powder Mill Road, Adelphi, MD 20783

FA6. (9:4))

ANALYSIS OF THE ν_6 BAND OF CHD_2F

D. F. EGGERS AND J. W. C. JOHNS

A sample of CHD_2F has been synthesized, in isotopic purity above 95 %. The four fundamentals ν_4, ν_5, ν_6 and ν_9 all occur in the general region of CO_2 laser lines. Optical pumping of this substance results in FIR laser action on a number of lines;[1] some of the strongest ones are associated with absorption of the CO_2 pumping lines by the ν_6 band.

Assignments of the FIR emission lines will be discussed, along with progress on the analysis of the band. We show that one of the weak FIR lines from pumping CD_3F[2] is actually due to a small amount of CHD_2F present as an isotopic impurity. Further, some OODR signals from a sample of CD_3F[3] are also shown to be due to CHD_2F.

1. M. S. Tobin, private communication and to be published.
2. Tobin, Sattler and Wood, Opt. Lett. 4, 384 (1979).
3. G. Duxbury and H. Kato, Chem. Phys. 66, 161 (1982).

Address of Eggers: Department of Chemistry, BG-10, University of Washington, Seattle, WA, 98195.
Address of Johns: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A OR6.

FA7.

(10:10)

ANALYSIS OF ALLENE-D_4 BANDS IN THE 4.2 - 5.3 μm REGION

J. PLIVA, K. ROUSAN, AND S. R. POLO

The spectrum of allene-d_4 between 1880 and 2390 cm^{-1} was measured on a Bomem high resolution Fourier transform spectrometer and deconvolved to a linewidth of 0.0025-0.0028 cm^{-1}. The main bands in this region include the C=C stretching fundamental ν_6 (species B_2) and the two C-D stretching fundamentals ν_5 (B_2) and ν_8 (E), accompanied by the $\nu_2+\nu_7$ (B_2) combination band enhanced by Fermi resonance with ν_5. All the bands exhibit severe perturbations by numerous combination and overtone levels. The interacting states deemed responsible for the stronger perturbations were incorporated in the Hamiltonian and a rovibrational analysis of the observed spectrum was carried out with the aid of our computer program system SYMTOP. A much improved set of spectroscopic constants will be reported for the upper states of the fundamental bands and for some of the perturbing states. An accurate set of ground state constants will also be given.

Address of Pliva and Polo: Department of Physics, The Pennsylvania State University, University Park, Pennsylvania 16802.
Address of Rousan: Physics Department, Yarmouk University, Irbid, Jordan.

FA8.

(10:27)

INTENSITY AND BROADENING STUDIES OF PROPANE, ACETYLENE, METHYL CHLORIDE AND ETHANE IN THE 12-14μm REGION

W. E. BLASS, J. K. LAWSON, G. W. HALSEY AND M. A. DAKHIL

Tunable diode laser measurements of line strengths and pressure broadening coefficients (self and foreign gas) are being carried out on propane, acetylene, methyl chloride and propane. Current results will be presented.

Address of Blass, Lawson, Halsey and Dakhil: Molecular Spectroscopy Laboratory, Department of Physics and Astronomy, The University of Tennessee, Knoxville, TN 37996-1200.

FA9.

(10:39)

DETAILED ANALYSIS OF THE 5μm ABSORPTION REGION OF $^{13}CD_3F$

G. W. HALSEY, J. A. DAKHIL AND W. E. BLASS

The 5μm region of the absorption spectrum of $^{13}CD_3F$ has been interpreted and analyzed in detail. The principle observed bands are ν_4, $2\nu_2$, $2\nu_5(\ell=0)$ and ν_1 with $\nu_2+\nu_5$, $\nu_2+\nu_3$, $\nu_3+\nu_5$, $2\nu_5(\ell=\pm2)$ interactions. A detailed discussion of the distribution of ν_1 band intensity due to various local and global interactions will be presented.

Address of Halsey, Dakhil and Blass: Molecular Spectroscopy Laboratory, Department of Physics and Astronomy, The University of Tennessee, Knoxville, TN 37996-1200.

FA10. (10:50)

ANALYSIS OF $2\nu_2$ BAND OF $^{12}CD_3F$

M. A. DAKHIL, G. W. HALSEY, AND W. E. BLASS

In the process of studying the 5-micron spectrum of $^{12}CD_3F$, the $2\nu_2(A_1)$ band has been assigned for the first time. More than 350 transitions have been assigned. This band interacts with ν_4 through a Coriolis interaction which causes crossings in the k = 5 to k = 8 sub-bands. Interpretation and analysis will be discussed.

Address of Dakhil, Halsey and Blass: Molecular Spectroscopy Laboratory, Department of Physics and Astronomy, The University of Tennessee, Knoxville, TN 37996-1200.

FA11. (11:08)

THE HIGH RESOLUTION SPECTROSCOPY OF CYCLOPROPANE $\nu_9 + \nu_{10}$ COMBINATION BAND PERTURBED BY FERMI AND CORIOLIS RESONANCES

ZHU QINGSHI, SHEN ZHIYE, SHEN HUIHUA, LIU HUIFANG, ZHANG BAOSHU, HUANG RUNLAN, and ZHANG CUNHAO

The combination band $\nu_9 + \nu_{10}$ of cyclopropane was found, the band center is 2464.52 cm^{-1}, it's FTIR and diode laser spectroscopy studies are reported here. The transitions are assigned and least square fitted to estimate the molecular constants. The anomalies observed in the rotational structure of $\nu_9 + \nu_{10}$ band are attributed to the Fermi and Coriolis interactions between $\nu_9 + \nu_{10}$ and $\nu_2 + \nu_{10}$, $\nu_5 + \nu_9$, and the ℓ-type *resonances. The J-structures* of $Q_K(J)$'s in the diode laser spectrum display very clearly a variation of $(B'-B_0)$ as a function of K which provides a good example for the study on this type of effect of Fermi resonance.

Address of Zhu Qingshi: Salt Lake Institute of Chinese Academy of Sciences, Sining, Qinghai, People's Republic of China.
Address of other authors: Dalian Institute of Chemical Physics, Dalian, People's Republic of China.

FA12. (11.25)

VISIBLE AND NEAR INFRARED SPECTRA OF CYCLOPROPANE*

S. L. BRAGG

The spectrum of gaseous cyclopropane, C_3H_6, has been observed between 10,000 and 16,000 cm^{-1} with a high resolution Fourier Transform Spectrometer at a pressure of 13.3 kPa (100 Torr). The 4-0 and 5-0 vibrational overtone bands of the C-H stretch have been observed using a local mode model[1] to assign the spectrum, and absolute absorption cross sections have been measured. *The 4-0 band has not previously been observed.*

The 5-0 band has recently been used as the standard for photoacoustic cell calibration.[2] The maximum absorption cross section for this band, at 14055.1 cm^{-1} is ~ 5.2×10^{-24} cm^2. This band is ideally suited for photoacoustic cell calibration because it is broad and contains no rotational line structure. It is easily accessible with a dye laser, and variations in the laser frequency and bandwidth will be unimportant in the calibration. In addition, the fast vibration-translation relaxation rates guarantee complete thermalization of the absorbed energy.

*This work was supported in part by AFWL Contract F29601-82-C-0019 and supported in part under the McDonnell Douglas Independent Research and Development Program.

1. R. G. Bray, SPIE Vol. 286, Laser Spectroscopy for Sensitive Detection, pp 9-17 (1981).
2. S. A. Lawton, S. L. Bragg and C. E. Wiswall, "Absorption Spectra of Atmospheric Gases Near the 1.315 μm Iodine-Atom Laser Line", Proceedings of the Lasers '82 Symposium (in press).

FA13. (11:37)

FIRST OBSERVATION OF $^{12}C_2H_4$ AND $^{12}C^{13}CH_4$ HOT BANDS IN THE 10 µm REGION

L. HENRY, A. VALENTIN, M. DE VLEESCHOUWER, Ch. LAMBEAU and A. FAYT

Fourier Transform spectra of heated (230°C) $^{12}C_2H_4$ and $^{12}C^{13}CH_4$ ethylenes have been recorded from 840 to 1040 cm^{-1} using the F.T. Spectrometer of the Laboratoire de Spectronomie Moléculaire with an apparatus function of $4\times10^{-3} cm^{-1}$ (F.W.H.M.) and an absolute precision of $2\times10^{-4} cm^{-1}$.

The quality of the spectra yields to the first observation of the three most intense hot bands of both isotopes. These hot bands, $\nu_7+\nu_{10}-\nu_{10}$, $\nu_7+\nu_8-\nu_8$ and $2\nu_7-\nu_7$, are involved in the optical pumping processes of ethylene with CO_2 and N_2O lasers.

Furthermore, for $^{12}C_2H_4$, the analysis of the $\nu_7+\nu_8$ band on the basis of F.T. Spectra* combinated with the observation of the $\nu_7+\nu_8-\nu_8$ band leads to the full determination and the analysis of the isolated Raman active ν_8 level with an accuracy better than 0.001 cm^{-1}. The study of $\nu_7+\nu_{10}$ and $2\nu_7$ is much more complicated because they are strongly coupled with at least five other levels. The analysis model will be discussed.

* Ch. LAMBEAU, M. DE VLEESCHOUWER, A. FAYT and G. GUELACHVILI to be published.

Address of L. HENRY and A. VALENTIN: Laboratoire de Spectronomie Moléculaire, Universite Pierre et Marie Curie, F-75230 PARIS, Cedex 05, FRANCE.
Address of M. DE VLEESCHOUWER, Ch. LAMBEAU and A. FAYT: Department of Molecular Spectroscopy, University of Louvain, Chemin du Cyclotron, 2, B-1348 LOUVAIN-LA-NEUVE, BELGIUM.

FA14. (11:54)

HIGH VIBRATIONAL OVERTONES IN $SiHCl_3$ AND SiH_2Cl_2

R. A. BERNHEIM, F. W. LAMPE, J. F. O'KEEFE, AND J. R. QUALEY, III

Absorption spectra in the 12 000 cm^{-1} to 18 000 cm^{-1} range have been recorded for gaseous $SiHCl_3$ and SiH_2Cl_2 using intracavity photoacoustic detection and CW dye lasers. The observed transitions correspond to the Δv = 6,7,8 and 9 overtones of the Si-H stretch and are adequately interpreted in terms of a local mode description of the vibration. Anharmonic constants of 35.0 cm^{-1} for $SiHCl_3$ and 34.4 cm^{-1} for SiH_2Cl_2 are found from a Birg-Sponer plot of the higher overtones. The band shape structures are consistent with parallel bands for $SiHCl_3$ and a B/C hybrid for SiH_2Cl_2.

Address: Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania, 16802.

FA15. (12:06)

MOLECULAR CONSTANTS OF SEVERAL LEVELS OF ISOTOPIC CARBON DISULFIDE FROM IR SPECTRA

ROMOLA D'CUNHA, JON MANHEIM, K. NARAHARI RAO, and C. J. SELISKAR

The Fourier Transform spectra of isotopically enriched carbon disulfide have been obtained with a resolution of 0.01 cm^{-1} at the Kitt Peak National Observatory.* The $(\nu_1 + \nu_3)$ combination bands in the region 2100-2250 cm^{-1} of several isotopic species particularly $^{12}C^{32}S^{34}S$, $^{12}C^{32}S^{33}S$, $^{12}C^{32}S_2$ and $^{13}C^{32}S_2$ have been reinvestigated. Due to the better resolution in the present studies, closely spaced lines could be resolved, leading to better determined molecular constants. Two new band systems $02^01 \leftarrow 00^00$ and $03^11 \leftarrow 01^10$ of $^{12}C^{32}S^{34}S$ have also been identified and analyzed. The ℓ-type doubling in the Π-Π band was found to be resolved for lines with $J > 13$, and the ℓ-type doubling constants for the 01^10 and 03^11 states of $^{12}C^{32}S^{34}S$ have been obtained.

*We are grateful to J. W. Brault and R. Hubbard who enabled us to obtain the spectra.

Address of D'Cunha, Manheim, and Rao, Department of Physics, The Ohio State University, Columbus, Ohio, 43210.

Address of Seliskar, Department of Chemistry, University of Cincinnati, Cincinnati, Ohio, 45221.

Permanent address of Manheim, Wright Patterson Air Force Base, Ohio, 45433.

Permanent address of D'Cunha, Spectroscopy Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India.

FA16. (12:11)

OBSERVATION AND ANALYSIS OF THE FUNDAMENTAL BENDING MODE OF T_2O

H. A. FRY, L. H. JONES, and J. E. BAREFIELD

The absorption spectrum of T_2O has been observed at 0.04 cm^{-1} resolution using a Fourier transform infrared spectrometer. 549 transitions in the ν_2 band centered at 995.326 have been assigned. 474 of these transitions were included in a fit in which the excited vibrational state constants were allowed to vary and the ground state constants hold fixed at values determined from microwave data. A Watson Hamiltonian with an AS reduction in a 3R representation was used for analysis. The terms retained in the rotational Hamiltonian for the ground state included up to tenth order distortion constants while the Hamiltonian of the excited vibrational included only terms up to eighth order. The standard deviation of the fit was 0.008 cm^{-1}.

Address: Los Alamos National Laboratory, Los Alamos, New Mexico, 87545.

FB1.

(8:30)

"BEST" SPECTROSCOPIC CONSTANTS FOR HgBr FROM DIRECT FITS OF MULTIPLE BAND SYSTEMS TO POLYNOMIALS AND NEAR-DISSOCIATION EXPANSIONS*

J. GAIL ASHMORE AND JOEL TELLINGHUISEN

The B→X (4200-5100 Å), C→X (2700-2950 Å), and D→X (2480-2700 Å) transitions of HgBr have been photographed and analyzed for isotopically pure $^{200}Hg^{79}Br$ and $^{200}Hg^{81}Br$. The analyses yield improved vibrational constants for all four states and rotational constants for the B and X states. Optimal spectroscopic parameters are obtained for all four states from direct, simultaneous fits of all three transitions to the standard polynomials in (v+1/2) and to near-dissociation expansions.[1,2]

In addition to the above-mentioned systems, we have recorded and analyzed by computer simulation the B→A transition (5500-8000 Å). Efforts are currently underway to (1) measure collisional line broadening in the B→X system using a Fabry-Perot interferometer, and (2) determine the R-dependence of the B→X transition strength function from analysis of relative intensity data.

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* Work supported by the Office of Naval Research.
[1] R. J. Le Roy and W-H. Lam, Chem. Phys. Lett. 71, 544 (1980).
[2] J. Tellinghuisen, J. Chem. Phys. (in press).

Address of Authors: Department of Chemistry, Vanderbilt University, Nashville, TN 37235.

FB2.

(8:47)

INTERFACING A MICRODENSITOMETER TO A MICROCOMPUTER*

O. CARLYSLE SALTER AND JOEL TELLINGHUISEN

In methods of photographic spectroscopy there is a need for precision measurement of a large amount of experimental data -- the positions and intensities of rotational lines, vibrational band heads, and calibration lines on the photographic plate. Microdensitometers and optical comparators permit one to measure the positions of sharp features with a precision of 1-2 μm; however, the procedure of measuring, recording, and logging the data for further computer processing can be very tedious and time consuming, if done manually. To expedite this aspect of our work, we have designed and built a cheap (~$2500, microcomputer included) control interface, by means of which a TRS-80 Model III microcomputer controls the motion of the plate on a microdensitometer and logs the optical density in digital form. In this paper we discuss various aspects of the interfacing task, including hardware and software for stepping motor control, analog-to-digital conversion, and extraction of line positions from the recorded data.

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* Work supported by the Office of Naval Research.

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FB3. (9:04)

REFLECTION AND INTERFERENCE STRUCTURE IN DIATOMIC FRANCK-CONDON DISTRIBUTIONS*

JOEL TELLINGHUISEN

Loosely speaking, the Franck-Condon distributions for diatomic radiative transitions from a single vibrational level of a given electronic state to all possible levels (bound and free) of a second electronic state exhibit either "reflection" or "interference" structure. In reflection structure there is a one-to-one mapping of peaks in the initial state probability distribution into peaks in the spectrum. No such simple relationship is known for interference structure (originally called "internal diffraction" by Condon[1]). It can be shown that the condition for reflection structure is a monotonic difference potential in the range of internuclear distance R sampled by the initial wavefunction, whereas interference structure occurs when the initial wavefunction samples extrema in the difference potential.[2] These conditions are discussed with application to a number of diatomic transitions.

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* Work supported by the Air Force Office of Scientific Research.
[1] E. U. Condon, Phys. Rev. 32, 858 (1928).
[2] J. Tellinghuisen, et al., Chem. Phys. 50, 31 (1980).

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FB4. (9:21)

THE 2880-Å EMISSION SPECTRUM OF I_2: ION-PAIR STATES NEAR 47,000 CM^{-1} *

K. S. VISWANATHAN AND JOEL TELLINGHUISEN

In the emission spectrum of I_2 in Ar, the second most intense band is a narrow peak near 2880 Å accompanied by several progressively weaker shoulders and peaks extending to 2830 Å.[1] At low resolution this system strongly resembles the bound-free B→X and D→X emission bands of the rare gas halides.[2] Under high resolution and with the use of a "cool" discharge, this system displays fine violet-degraded band structure. The analysis of the vibrational structure indicates that the transition originates from an ion-pair excited state and terminates on a weakly bound lower state which dissociates to two ground-state atoms. By a process of elimination we arrive at the probable designation, $0_g^-(^3P_1) \rightarrow 2431\ 0_u^-(^3\Pi)$. According to this interpretation the upper state is the fourth of six predicted ion-pair states near 47,000 cm^{-1} to be identified experimentally, and the lower state is the last case c component of the lowest $^3\Pi$ state to be observed.

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* Work supported by the Air Force Office of Scientific Research.
[1] A. L. Guy, et al., Chem. Phys. Lett. 73, 582 (1980).
[2] J. Tellinghuisen, et al., J. Chem. Phys. 65, 4473 (1976).

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FB5. (9:38)

CYBERNETIC REANALYSIS OF THE S_2 $B\,{}^3\Sigma_u^- - X\,{}^3\Sigma_g^-$ TRANSITION

GEORGE V. [illegible]ANSKY AND ALLAN L. SMITH

This work presents the current status of our ongoing effort to understand the strong perturbations in disulfur's $B\,{}^3\Sigma_u^-$ state and ultimately to derive deperturbed energy levels of both the B state and the perturbing $B''\,{}^3\Pi_u$ state. The approach taken is the utilization of cybernetics - the marriage of man's power of pattern recognition and of the computer's power of numerical manipulation wherein the scientist is the controlling element in the man-machine interrelationship.

The cybernetic approach required the generation of a database of all available assigned S_2 B-X spectral lines (about 10,000 lines from 50 vibrational bands) and the development of graphics-oriented software to support database manipulation and spectral analysis. The reanalysis used both traditional spectroscopic methods (Fortrat diagrams, complete sets of combination relations) and statistical methods (regression, Grubb's point rejection method[1]) to generate tables and tableaus from which the scientist verifies or corrects rotational analyses. An intermediate result of this analysis is a new database of $B\,{}^3\Sigma_u^-$ state term values and a three-dimensional plot of v' versus J' versus energy for levels of each parity.

The use of relational database management software in spectroscopic problems will also be discussed, and a preliminary deperturbation effort will be presented.

1. Frank E. Grubbs, "Procedures for Detecting Outlying Observations in Samples", Technometrics 11, 1 (1969)

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FB6. (10:05)

VARIATION OF THE ELECTRONIC TRANSITION MOMENT IN THE A $^2\Pi$ - X $^2\Pi$ SYSTEM OF CLO

S. A. BARTON, J. A. COXON AND U. K. ROYCHOWDHURY

The v" = 0 progression of the A $^2\Pi$ - X $^2\Pi$ system of ClO has been recorded photoelectrically in the first order of 2400 grooves/mm grating using a 1.26m spectrometer. ClO was generated in a fast flow system at near room temperature and 1.5 mm Hg total pressure. Continuum radiation from a Xe arc source was passed back and forth along a 1m flow tube by means of an external arrangement of concave mirrors.

The line positions for each of the recorded bands ($3 \le v' \le 12$) were computed from the available constants for the X- and A-states[1]. Absorption cross section profiles for individual bands were then generated from the known Franck-Condon factors[2] and trial values of temperature, linewidth and band strength. Synthetic absorption profiles for the recorded bands were then obtained readily by convolution with the known triangular slit function. A non-linear least squares routine was applied iteratively to obtain improved estimates of the temperature, linewidth and band strength as well as two additional parameters which served to calibrate the spectra against the known ClO (A - X) wave numbers. The matching of the experimental data and the synthetic absorption profiles is excellent for all bands. A smooth variation of the electronic transition moment with upper state vibrational quantum number has been established. The linewidths are about twice those estimated approximately from photographic plates by Coxon and Ramsay[3].

The parameters obtained in the present work could be used to generate reliable synthetic absorption spectra for the longer wavelength v" = 0 bands under stratospheric conditions. Comparison with experimental data might then provide a means for continuous measurement of absolute ClO concentrations in the stratosphere.

[1]J. A. Coxon, W. E. Jones and E. G. Skolnik, Can. J. Phys. 54, 1043 (1976).
[2]J. A. Coxon, J. Photochem. 6, 439 (1976/77).
[3]J. A. Coxon and D. A. Ramsay, Can. J. Phys. 54, 1034 (1976).

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FB7. (10:22)

ROTATIONAL ANALYSIS OF THE A $^2\Pi \rightarrow X\ ^2\Pi$ SYSTEM OF THE SULPHUR MONOXIDE CATION

J. A. COXON AND S. C. FOSTER

The visible A → X emission system of SO^+ is excited by the reaction of He^+ ions with SO_2 in a fast flow system. Several bands of the v' = 0 and v' = 1 progressions have been recorded photoelectrically using a 1.26 m spectrometer operated under computer control. The bands are free of any overlapping structure from other emitters, and the rotational structure is well resolved.

Direct least-squares reduction of the measured wavenumbers using merging techniques[1,2] leads to well determined estimates of the rotational and spin orbit coupling constants in both states, which complement those from the photographic study of Cossart et al[2].

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[1]D. L. Albritton, A. L. Schmeltekopf and R. N. Zare, J. Mol. Spectrosc. 67, 132 (1977).
[2]J. A. Coxon, J. Mol. Spectrosc. 72, 252 (1978).
[3]D. Cossart, H. Lavendy and J. M. Robbe, to be published.

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FB8. (10:39)

ROTATIONAL ANALYSIS OF THE B $^2\Sigma^+ \rightarrow X\ ^2\Sigma^+$ SYSTEM OF ALO

J. A. COXON and S. NAXAKIS

The B $^2\Sigma^+ \rightarrow X\ ^2\Sigma^+$ "blue-green" band system of AlO was excited in a microwave discharge through a flow of aluminum chloride and trace quantities of oxygen.
Twenty-five bands with $0 \leq v' \leq 9$ and $0 \leq v'' \leq 7$ have been photographed at high resolution and rotationally assigned. Band origins, effective rotational parameters (B,D), and spin-rotation coupling constants (γ) of the model Hamiltonian used to describe individual vibrational levels of both states, are determined by linear least-squares fitting of the data of each band. Multiple estimates of the parameters are merged to obtain the best single-valued estimates of the same parameters, as well as Dunham coefficients describing their vibrational dependence. The vibrational dependence of γ' for the B-state is linear in v'; for the ground state, no significant dependence of γ'' could be established.

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FB9. (10:57)

POPULATION ANOMALIES IN AN Mg + N_2O FLAME

P.C.F. IP, JEFFREY A. GRAY, K. CROSS, AND R.W. FIELD

Intensity anomalies were observed from the spectroscopic analysis of the MgO $B^1\Sigma^+$ - $a^3\Pi_i$ system..Information on population was obtained using linestrength factors calculated from the $X^1\Sigma^+$ - $a^3\Pi$ - $A'\Pi$ deperturbation. The population ratios of $a^3\Pi$ to $A^1\Pi$ and of $a^3\Pi$ e- to f-parity were found to be more than a factor of two greater than those expected from a Boltzmann distribution.

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FB10. (11:05)

THE CaO $c^3\Sigma^+$ - $a^3\Pi_i$ SYSTEM

J.B. NORMAN, K.J. CROSS, H.S. SCHWEDA, R.F. BARROW, R.W. FIELD

A portion of the CaO "Second Orange Arc Band System" (617-627nm) has been assigned as the 0,0 band of the $c^3\Sigma^+$-$a^3\Pi_i$ transition. $c^3\Sigma^+$ is derived from a $\pi^3\pi'$ configuration and is isoconfigurational with the recently observed D,$d^{1,3}\Delta$ state.[1]

Sub-Doppler spectroscopy is required to resolve the dense rotational structure. Intermodulation spectroscopy has been employed.

The band system has been observed in a Ca + O_3 flame. It originates in the same lower electronic and vibrational states as another prominent CaO band system recently observed in a Ca + N_2O + CO flame. However, no part of the "Second Orange Arc Band System" has been observed following the latter reaction.

This investigation has yielded $B_0(c^3\Sigma^+) = 0.350$ cm^{-1} and $^RQ_{23}(1) = 16165.7$ cm^{-1}. The latter value compares favorably with that predicted by Bauschlicher and Yarkony (16500 cm^{-1})[2] for the location of $c^3\Sigma^+$ relative to $a^3\Pi$.

[1] R.F. Marks, H.S. Schweda, R.A. Gottscho, and R.W. Field, J. Chem. Phys. 76, 4689 (1982).

[2] C.W. Bauschlicher, Jr. and D.R. Yarkony, J. Chem. Phys. 68, 3990 (1978).

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FB11. (11:25)

CW Ion Laser Excitation of OH and NH in an Atmospheric Pressure Flame

J.A. VANDERHOFF, A.J. KOTLAR, and W.R. ANDERSON

Intense laser fluorescences of the important NH and OH radicals in a flame have been observed upon excitation by the 3507Å line of a krypton ion laser. The experimental apparatus was very similar to that described in detail previously[1] for use in laser Raman and fluorescence flame investigations. Briefly, a lean $CH_4/N_2O/N_2$ flame (~2500K flame temperature) was placed inside the extended cavity of a 3 W (all lines) krypton laser with prism tuned line selection. Fluorescence excited by the laser was detected by a 25 cm monochromator equipped with a silicon intensified vidicon tube. When the laser was tuned to 3507Å, intense fluorescences of NH and OH above the flame emission were observed. A simple differencing technique allowed for removal of the flame emission from the fluorescence spectra. The fluorescence spectra, combined with detailed calculation of line positions, lead to the following tentative assignments of pumping transitions:

NH, A-X (0,0) $^OP_{23}$ 21;

OH, A-X (0,1) Q_1 19.

However, some ambiguity still exists concerning these assignments. The observed spectra and assignments will be discussed.

[1] W.R. Anderson, J.A. Vanderhoff, A.J. Kotlar, M.A. DeWilde, and R.A. Beyer, J. Chem. Phys., 77, 1677 (1982).

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FB12. (11:37)

SPECTROSCOPY OF THE $He^*(2^3S)-C_2H_2$ FLAME

D.H. WINICUR, J.H. HARDWICK, S.N. MURPHY

A detailed study has been made of the spectroscopy of the products of the electronically-excited, metastable $He^*(2^3S) + C_2H_2$ reaction. A D.C.-discharge diffusion flame technique is used, which affords a highly selective method for producing and studying the fluorescence of gas-phase radicals.

The products observed are C_2^*, CH^*, H^*, and C^*. The reaction, $He^* + C_2H_2 \rightarrow C_2^* + H + He$, produces an extremely bright source of C_2 fluorescence over the entire optical range and many Swan ($d^3\Pi_g - a^3\Pi_u$) and Fox-Herzberg ($e^3\Pi_g - a^3\Pi_u$) bands have been observed for the first time. Several bands of the C_2 Fox-Herzberg system in the near ultraviolet have been recorded at higher resolution than has previously been reported. These bands have been analyzed in an attempt to extract spin-orbit coupling constants for the excited state. Concurrently, bands of the Swan system have been rephotographed in order to confirm and improve ground-state combination differences.

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FB13. (11:54)

High Resolution Laser Spectrum of the Second Positive Band System of N_2 Under Electron Beam Excitation

PUTCHA VENKATESWARLU and S. K. BASU

The high resolution spectrum of the second positive band system of N_2 has been recently reinvestigated by Venkateswarlu, Murthy and Basu using a transversely excited segmented electrode nitrogen laser tube just below and just above laser threshold. In the present work, nitrogen at a pressure of 3 torr was excited by a Febetron 706 electron beam (400 KeV) generator using 3 ns pulses. Spectra were taken using a vacuum Ebert spectrograph in the 17th and 18th orders at dispersion of about 0.1A°/mm. The rotational structure of the 0-0, 0-1 and 1-0 laser bands has been studied. More R branch lines are found to lase than those recorded earlier. Mixtures of N_2 and He at relative pressures of 3-10 torr of N_2 and 10 to 20 torr of He have been excited with the electron beam to study selective excitations in the rotational spectrum. It was found that the rotational line Q_3 (2) lases at the expense of the line R_3 (4). The energy separation between the lower levels J = 4 and J = 2 of these lines is about 25 cm^{-1} which corresponds to the separation between 13s ^1S and ^3S of He suggesting an energy transfer between He and N_2 to be responsible for the selective excitation of the Q_3 (2) over R_3 (4).

---

1. P. Venkateswarlu, A. N. Murthy and S. K. Basu, Ind. J. Phys., 54B, 388 (1980)

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FC1. (6:30)

STRUCTURE OF LiNC BY MOLECULAR BEAM ELECTRIC RESONANCE SPECTROSCOPY

J.J. van Vaals, W. Leo Meerts, and A. Dymanus

The rotational spectrum of LiNC has been measured for the first time. We succeeded in producing a supersonic molecular beam (1% LiNC in Ar). The LiNC molecule has been produced in two totally *different chemical reactions*. Two rotational transitions in the ground vibrational state at 26.6 and 53.2 GHz were observed, being $J = 1 \leftarrow 0$ and $J = 2 \leftarrow 1$. The hyperfine structure was resolved and identified using microwave double resonance. The results for the rotational constants are: B_e = 13293.293(3) MHz, D_e = 32.5(4) kHz; the quadrupole coupling constants are: eqQ(Li) = 0.366(30) MHz, eqQ(N) = 2.944(10) MHz. The $J = 1 \leftarrow 0$ rotational transition of ^{6}LiNC at 29.2 GHz was observed in natural abundance, yielding B_e = 14591.504(20) MHz.

From this we can conclude that LiNC has a *linear* isocyanide structure. In earlier work we observed the rotational spectrum of KCN and NaCN and we found surprisingly a *T-shaped* structure for both molecules.

The results for the effective structural parameters are: r_{LiN} = 1.760 Å, and r_{NC} = 1.168 Å. We did not observe transitions of excited vibrational states or LiCN (abundance in the beam ≤ 3%). This leads to an estimated isomerization energy ≥ 120 cm^{-1}. The agreement between our experimental results and recent *ab initio* calculations is good.

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FC2. (3:47)

ROTATIONAL-VIBRATIONAL STATE DEPENDENCE OF NUCLEAR QUADRUPOLE INTERACTIONS IN DIATOMIC MOLECULES, **JAMES CEDERBERG AND DAVID NITZ**

In the context of the Born-Oppenheimer approximation, one should expect the electric field gradient at a nuclear site to depend on the internuclear distance. Expanding this function about the equilibrium distance and averaging over rotation-vibration would then give

$$q(v,J) = q_e + q_1\langle\xi\rangle + q_2\langle\xi^2\rangle + \ldots,$$

where $\xi = (r-r_e)/r_e$. We have evaluated the averages after the manner of Dunham's energy expansion, and find

$$\langle\xi^n\rangle = \sum_{lm} Z^n_{lm}(v+1/2)^l[J(J+1)]^m,$$

where, to second order in B_e/ω_e,

$$Z^1_{00} = (-15a_3/4 + 23a_1a_2/4 - 21a_1^3/8)(B_e/\omega_e)^2 \qquad Z^1_{10} = -3a_1(B_e/\omega_e)$$

$$Z^1_{20} = (-15a_3 + 39a_1a_2 - 45a_1^3/2)(B_e/\omega_e)^2 \qquad Z^1_{01} = 4(B_e/\omega_e)^2$$

$$Z^2_{00} = (-3a_2/2 + 7a_1^2/4)(B_e/\omega_e)^2 \qquad Z^2_{10} = 2(B_e/\omega_e)$$

$$Z^2_{20} = (-6a_2 + 15a_1^2)(B_e/\omega_e)^2 \qquad Z^3_{00} = (-7a_1/4)(B_e/\omega_e)^2$$

$$Z^3_{20} = -15a_1(B_e/\omega_e)^2 \qquad Z^4_{00} = (3/2)(B_e/\omega_e)^2$$

$$Z^4_{20} = 6(B_e/\omega_e)^2.$$

This prediction is tested against experimental data for HCl and KCl.

This work is supported in part by a Northwest Area Foundation Grant of Research Corporation.

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FC3. (8:59)

HYPERFINE SPECTRUM OF KCL AS OBSERVED BY MOLECULAR BEAM ELECTRIC RESONANCE SPECTROSCOPY, DAVID NITZ, JAMES CEDERBERG, KEITH HETZLER, ARTHUR KOTZ, AND STANLEY TEAD

We have observed weak-field hyperfine transitions in KCl for vibrational-rotational states (v,J) = (0, 2-9) and (1, 2-4) using a high resolution molecular beam spectrometer. Linewidths of the observed transitions are 200 Hz (FWHM). Analysis of the (v,J) = (0,2) data yields the following set of hyperfine interaction constants for the $^{39}K^{35}Cl$ isotope (in units of kHz):

$$(eqQ)_K = -5664.74 \ (5)$$

$$(eqQ)_{Cl} = 56.2 \ (5)$$

$$c_K = 0.035 \ (10)$$

$$c_{Cl} = 0.46 \ (1)$$

$$d_T = 0.07 \ (2)$$

$$d_S = -0.01 \ (2)$$

The quadrupole constants lie outside the experimental uncertainties of previously-reported measurements made at lower resolution and high field on the J = 1 state.[1] Analysis of the higher rotational and vibrational states is in progress.

[1]R. van Wachem and A. Dymanus, J. Chem. Phys. 46, 3749 (1967).

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FC4. (9:11)

VIBRATIONAL RELAXATION OF LINEAR MOLECULES IN SUPERSONIC EXPANSIONS

R. L. DeLEON AND J. S. MUENTER

The question of vibrational cooling in a supersonic nozzle expansion has been investigated for the case of a 25 micron diameter nozzle using Ar as the carrier gas. The relative populations of thermally excited vibrational states were estimated from the intensities of radio frequency transitions in OCS, HCN, and cyanoacetylene. Using molecular beam source temperatures ranging from 300 to 825° K, 12 states having from 200 to 2100 cm^{-1} vibrational excitation have been studied. Typical expansion conditions were 10% linear molecule in 90% Ar at 2 atmospheres pressure and a source temperature just high enough for adequate sensitivity. Comparison of ground state with excited state radio frequency transition intensities permitted and excited vibrational state temperature to be measured to an accuracy of better than ± 20%. To compare the results for different experiments the vibrational temperature was divided by the source stagnation temperature and these reduced temperatures ranged from .3 to 1. The reduced rotational temperature was estimated to be .05. These data were fit to $1-\exp(-\omega/C)$ giving $C = 325 \pm 50$ cm^{-1}. Thus, vibrations with energy greater than 325 cm^{-1} are essentially uncooled while substantial cooling occurs for $\omega < 325$ cm^{-1}.

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FC5. (9:28)

MBER SPECTROSCOPY OF IR LASER EXCITED VIBRATIONAL STATES

WILLIAM EBENSTEIN AND J. S. MUENTER

Conventional molecular beam electric resonance spectroscopy has been carried out on molecules which have been excited with a color center laser. Initial experiments were done on the C-H stretch of HCN at 3300 cm^{-1}. A Burleigh FCL-20 laser e.cited the molecular beam either following the A field or immediately after the beam source. Approximately 10% of the available molecules were excited on a single pass. The laser was used without stabilization and radio frequency transitions were obtained in the excited state by scanning the RF frequency more rapidly than the laser drifted. Signal averaging was used to accumulate the rapid scans and sensitivity of excited state measurements were within a factor of ten of ground state sensitivity. Line shape for the excited state measurements were identical to ground state results. For HCN μ_v/μ_{gs} = 1.0108 and eqQ_v/eqQ_{gs} = .9901.

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FC6. (9:40)

DIPOLE MOMENTS OF EXCITED VIBRATIONAL STATES OF HCN

R. L. DeLEON AND J. S. MUENTER

Several techniques have been used to measure the dipole moments of 6 vibrational states of HCN. Conventional molecular beam electric resonance spectroscopy can readily observe the ground state and the 010 and 020 excited bending modes. A high temperature supersonic nozzle beam source was used to make MBER measurements on the 001 state, the C-N stretch. Infrared laser excitation of the molecular beam gave access to the 100 state (C-H stretch). The same laser was used in a gas phase RF-IR double resonance experiment to study the 110 state. These data will be discussed in terms of the dipole moment function of HCN.

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FC7. (10:10)

ROTATIONAL SPECTRA AND STRUCTURES OF H_2O-CO_2, $HDO-CO_2$ AND D_2O-CO_2

K.I.PETERSON, T.A.FISHER, AND W.KLEMPERER

Water-carbon dioxide complexes are formed in a supersonic expansion and their rotational spectra are measured between 0.5 MHz and 18 GHz using a molecular beam electric resonance spectrometer. Rotational constants are obtained from the data along with other structural information. The geometry is T-shaped and planar (C_{2v} symmetry) with the oxygen in the water bound to the carbon and the hydrogens directed away from the CO_2. Other parameters are given in the following table. The C - O distance is determined by optimizing a planar structure to fit B + C.

	H_2O-CO_2	$HDO-CO_2$	D_2O-CO_2
B + C (MHz)	7978.562 (10)	7605.216 (50)	7265.550 (50)
B - C (MHz)	1369.455 (20)	1260.318 (10)	1166.385 (50)
Dipole Moment (D)	1.8515 (10)	1.8911 (10)	1.9285 (10)
C - O Distance (A)	2.836	2.826	2.821

A spectrum calculated using a semirigid rotor model does not reproduce the observed transitions within experimental error but the difference between the observed and calculated values is within a few hundred kHz in each case. The presence of hindered internal rotation is inferred.

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FC8. (10:27)

THE MYSTERY OF ArHCN

G.T. FRASER, K.R. LEOPOLD, F.J. LIN, AND W. KLEMPERER

The rotational spectrum of the K=0 levels of the van der Waals complex ArHCN has been obtained by molecular beam electric resonance spectroscopy in an argon expansion. For ArHCN the $J \rightarrow J+1$, $J=0$ to 4 transitions were observed while for ArDCN the $J \rightarrow J+1$, $J=0$ to 6 transitions were observed. The spectroscopic constants for the K=0 levels are:

	B(MHz)	D_J(kHz)	eqQ_a(N) (MHz)	μ_a(D)
ArHCN	1609.832(3)	170(5)	-2.842(14)	2.6272(19)
ArDCN	1574.8(1)	96(6)	-3.158(25)	2.7496(26)

The spectrum does not fit well to the linear rotor Hamiltonian $H=BJ(J+1)-D_J J^2(J+1)^2$. Furthermore, the derived centrifugal distortion constant D_J, and its change upon deuterium substition are unexpectedly large. The rotational constants are consistent with an average structure in which the hydrogen points toward the argon. The average distance between the argon and the center of mass of the HCN is 4.34Å. The angle between the HCN axis and the a-axis as derived from both the dipole moment and quadrupole coupling is about 30°. Stretching and bending frequencies of ArHCN derived from the usual treatment are each 10cm^{-1} suggesting that excited levels should be populated in the beam and attempts are presently underway to observe transitions from these levels. The small bending and stretching frequencies are not understood since the bond strength of ArHCN must be greater than that of Ar_2 (D_e=100cm^{-1}, ω_e= 26cm^{-1})

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FC9. (10.44)

ROTATIONAL SPECTRA AND STRUCTURES OF $HCN-CO_2$ AND $DCN-CO_2$

K.R. LEOPOLD, G.T. FRASER, AND W. KLEMPERER

The rotational spectra of $HCN-CO_2$ and $DCN-CO_2$ were observed using the molecular beam electric resonance technique. The following spectroscopic constants were determined:

	$HCN-CO_2$	$DCN-CO_2$
A (MHz)	11861(12)	11670(230)
B+C (MHz)	4088.114(82)	3859.43(42)
B-C (MHz)	364.91(16)	323.4(2.8)
eqQ_a(N) (MHz)	-4.068(14)	-
Dipole Moment (D)	3.2005(60)	3.2235(55)

The molecule is T-shaped with the nitrogen bonded to the carbon of CO_2. The N-C van der Waals bond length is 3.01Å and the average angle between the a-axis and the HCN axis is 18°.

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FC10. (11:01)

DEUTERIUM QUADRUPOLE COUPLING CONSTANTS IN VIBRATIONALLY EXCITED HCCD: EVIDENCE FOR ELECTRON REORGANIZATION

M.D. MARSHALL AND W. KLEMPERER

The l-doubling spectra of monodeuteroacetylene have been obtained in the $v_4=1$ (C-D bend) and $v_5=1$ (C-H bend) states of the molecule with resolution sufficient to determine the deuterium nuclear quadrupole coupling constants. The spectroscopic constants obtained from the J=1 rotational level are:

		$v_4=1$	$v_5=1$
eqQ^D_{zz}	(kHz)	207. (6)	221. (2)
$eqQ^D_{xx} - eqQ^D_{yy}$	(kHz)	-31. (22)	-6. (4)
C_D	(kHz)	-6. (2)	-1.5(3)
C_H	(kHz)	---	-20.0(5)
μ	(D)	0.02359(11)	0.05624(3)
q	(MHz)	133.0506(9)	105.6993(2)

These results are in essential agreement with the microwave work of Hirota, et. al.[1] in which B_v was determined along with μ and the l-doubling constant.

A vector-tensor model of the electron distribution is used to discuss these results, and it is shown that they are inconsistant with the assumption of a cylindrical electron distribution about the C-D bond axis.

1.J. Phys. Chem., 84, 1793, (1980)

Address of Marshall and Klemperer: Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

FC11. (11:18)

THE ROTATIONAL ZEEMAN EFFECT IN THE ArOCS VAN DER WAALS COMPLEX

J. A. SHEA, W. G. READ, AND E. J. CAMPBELL

The rotational Zeeman effect has been measured in the weakly-bound complex ArOCS. The study was carried out on a pulsed Fourier-transform microwave spectrometer employing a supersonic nozzle and a Fabry-Perot cavity. The following spectroscopic constants were obtained:

$g_{aa} = -0.02483(21)$ $\quad 2\chi_{aa}-\chi_{bb}-\chi_{cc} = 1.313(32) \times 10^{-9}$ MHz/G^2

$g_{bb} = -0.00086(23)$ $\quad 2\chi_{bb}-\chi_{cc}-\chi_{aa} = -3.762(26) \times 10^{-9}$ MHz/G^2

$g_{cc} = -0.00558(11)$

Projection equations are used to relate the magnetic properties of free OCS to those of the complex. An analysis of the force field as obtained from centrifugal distortion is used to determine an average structure for ArOCS and mean square amplitudes of the van der Waals motions. These are used to augment the projection analysis. The molecular quadrupole moment of ArOCS is calculated from the Zeeman parameters. With an estimated bulk magnetic susceptibility, diamagnetic susceptibilities and the second moments of electronic charge distribution are also calculated.

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FC12. (11:30)

THE ROTATIONAL ZEEMAN EFFECT IN THE OCO-HF, OCO-DF, OCO-HCL, and SCO-HF COMPLEXES

J. A. SHEA, W. G. READ, AND E. J. CAMPBELL

The rotational Zeeman effect has been measured in the hydrogen-bound complexes OCO-HF, OCO-DF, OCO-HCl and SCO-HF. The zero-field rotational spectra of the isotopic species SCO-DF, ^{34}SCO-HF, O^{13}CO-HF, ^{18}OC^{18}O-HF, O^{13}CO-HCl, and ^{18}OC^{18}O-HCl have also been measured. The above studies were carried out on a pulsed Fourier-transform microwave spectrometer employing a supersonic nozzle and a Fabry-Perot cavity. The following spectroscopic constants were obtained:

	$g_\perp$	$\chi_{\parallel}-\chi_\perp$ (10^{-9} MHz/G^2)	B (MHz)	D_J (MHz)	χ_{aa} (MHz)	S_{aa} (MHz)
OCO-HF	-0.01393(27)	-1.39(19)	---	---	---	---
OCO-DF	-0.01384(12)	-1.16(10)	---	---	---	---
OCO-HCl	-0.005808(32)	-1.45(4)	---	---	---	---
SCO-HF	-0.01002(14)	-2.53(17)	---	---	---	---
SCO-DF	---	---	1290.7348(13)	0.01876(9)	0.242(10)	---
^{34}SCO-HF	---	---	1277.59298(3)	0.0023040(7)	---	---
O^{13}CO-HF	---	---	1939.7749(5)	0.01052(2)	---	0.101(4)
^{18}OC^{18}O-HF	---	---	1870.84244(5)	0.010031(2)	---	---
O^{13}CO-HCl	---	---	1099.7833(2)	0.004577(3)	-49.586(4)	---
^{18}OC^{18}O-HCl	---	---	1059.5772(1)	0.004288(2)	-49.65(4)	---

The Zeeman parameters are compared with values predicted by a set of equations which project the values of the individual subunits. The Zeeman parameters allow calculation of the quadrupole moment of each complex. With an estimated bulk magnetic susceptibility, diamagnetic susceptibilities and the second moments of the electronic charge distribution are also calculated.

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FD1. (8:30)

SINGLE CRYSTAL RAMAN SPECTRA OF MAGNESIUM AND ZINC PERCHLORATE HEXAHYDRATES

M. B. PATEL, ANSHU AGARWAL, AND H. D. BIST

Raman spectra of single crystals of $Mg(ClO_4)_2 \cdot 6H_2O$ and $Zn(ClO_4)_2 \cdot 6H_2O$ are presented for the first time in the region 20-4000 cm^{-1}. Ar^+ laser (514.5 nm) was used for excitation, and *polarization* studies were made in all the orientations of the crystals. The observed lines are attributed to the phonons originating from the Raman active modes of isolated $ClO_4^-(T_d)$ and $[M(OH_2)_6]^{2+}$ (T_h) units. The T_h symmetry considered for $[M(OH_2)_6]^{2+}$ complex is found consistent with the known crystal space group, C_{2v}^7, of the salts[1] and results in correct symmetry classification of *the 174 phonon* braches as $48A_1 + 39A_2 + 48B_1 + 39B_2$ in the unit cell. It is also shown that the water molecules lie almost in a plane perpendicular to the crystal c-axis.

[1] M. Ghosh and S. Ray, Z. Kristallogr. **145**, 146 (1977).

Address: Department of Physics, Indian Institute of Technology, Kanpur 208 016, India

FD2. (8:47)

INFRARED AND RAMAN SPECTRA OF MATRIX ISOLATED $(PbO)_n$ SPECIES

by,
Y.J. Park and R.K. Khanna

Department of Chemistry, University of Maryland
College Park, Maryland 20742

and
Bertram Donn

Goddard Space Flight Center, Greenbelt, Maryland 20771

Abstract

The infrared and Raman spectra of PbO vapor co-condensed with excess N_2 and Ar on a cold substrate (~ 12K) were investigated. The spectral changes accompanying the heat treatment (controlled warming for a specified period) of the sample were utilised to decipher the vibrational frequencies of monomeric and polymeric species. Normal coordinate treatment of the data enabled us to elucidate the structures of dimeric·trimeric and tetrameric species. A comparison with the results of SiO suggests different mechanisms of condensation in the two cases which will be discussed in this report.

FD3. (9:04)

VIBRATIONAL SPECTROSCOPIC STUDIES OF SO_3 IN SOLID STATE

by, G.V. Jere*, M. Ospina**, R.K. Khanna* and J. Pearl**

* University of Maryland, College Park, Maryland 20742

** Goddard Space Flight Center, Greenbelt, Maryland 20771

Abstract

Sulfur trioxide is an interesting molecule for vibrational spectroscopic studies because of its structural complexities in the condensed state. In this investigation sulfur trioxide was prepared by thermal decomposition of anhydrous Ferric sulfate and copper sulfate in vacuum (~ 10^{-6} torr). The evolved sulfur trioxide along with some sulfur dioxide was condensed on a Cesium Iodide plate at ~12K in a closed cycle helium cryo-cooler. Detailed analysis of the infrared and Raman spectra of the sample at several temperatures between 12K and 300K has enabled us to follow the phase changes in solid sulfur trioxide. Structural aspects of different phases of SO_3 will be described in this report.

FD4. (9:21)

RESONANCE RAMAN STUDIES OF GAS PHASE AND CONDENSED PHASE METALLOPORPHYRINS: TEMPERATURE DEPENDENCE OF VIBRATIONAL FREQUENCIES AND VIBRATIONAL ANHARMONICITIES

J. L. MURTAUGH AND S. A. ASHER

Metalloporphyrins are introduced into the gas phase by heating the porphyrins to 350°C under high vacuum. Resonance Raman measurements in conjunction with absorption spectroscopy and mass spectral studies indicate the Ni(II) octaethylporphin and Co(II) octaethylporphin are stable as four-coordinate gas phase species. The geometry of these gas phase porphyrins appear to be identical to that of the condensed phase species at similar temperature. Resonance Raman temperature dependent studies of both gas and condensed phase metalloporphyrins indicate a general lowering of the Raman frequencies as the temperature increases. These data suggest significant anharmonicities for low frequency porphyrin vibrations. The temperature dependent results will be related to the frequency shifts observed in recent photochemically generated transient Raman studies of heme proteins. In contrast to the Co and Ni porphyrins, ligated ferric porphyrins and manganese(III) etioporphyrin undergo internal oxidation-reductions as the samples are introduced into the gas phase. The metal is reduced while the ligand leaves as an atomic species. These results will be discussed in the context of porphyrin chemistry.

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FD5. (9:43)

DEVELOPMENT OF INSTRUMENTATION FOR TUNABLE UV RESONANCE RAMAN STUDIES IN THE 217-400 NM SPECTRAL REGION.

S. A. ASHER, C. R. JOHNSON, AND J. L. MURTAUGH

A new resonance Raman spectrometer tunable between 217-800 nm has been constructed for studies of aromatic molecules with absorption bands between 217-260 nm. The excitation source is a high-power Nd Yag laser which is frequency doubled or tripled, and pumps a dye laser, yielding tunable light between 370-800 nm. The dye laser light is either mixed with the 1.06 um Yag fundamental, frequency doubled, or frequency doubled and mixed with the 1.06 μm radiation to yield light between 217-420 nm. The spectrometer uses reflective collection optics to avoid chromatic aberrations and the Raman light is dispersed by using either a triple or high resolution modified double monochromator. The Raman scattered light is detected by using an intensified Reticon detector which is gated on during the 4 nsec Yag laser pulse. The gating decreases interference from sample fluorescence. The novel features of the instrument will be discussed in the context of the sampling methodologies required for UV resonance Raman measurements using pulsed laser excitation sources.

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FD6. (10.00)

UV RESONANCE RAMAN EXCITATION PROFILES OF BENZENE IN THE 217 TO 270 NM SPECTRAL REGION.

C. R. JOHNSON AND S. A. ASHER

Resonance Raman excitation profiles of benzene have been obtained in the 217-260 nm spectral region within the $^1B_{2u}$ benzene absorption band. The excitation profiles indicate a large intensity dependence as the excitation wavelength is tuned through the vibronic envelopes of the $^1B_{2u}$ electronic transition. The excitation profile of the 992 cm^{-1} benzene vibration will be discussed in the framework of current resonance Raman theory. The benzene excitation profiles will be compared to excitation profiles of other substituted aromatics. The utility of UV resonance Raman spectroscopy as a selective probe for aromatic residues in polymers and proteins will also be discussed.

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38TH MOLECULAR SPECTROSCOPY SYMPOSIUM AT THE OHIO STATE UNIVERSITY

	[illegible]DAY, JUNE 13TH	TUESDAY, JUNE 14TH	WEDNESDAY, JUNE 15TH	THURSDAY, JUNE 16TH	FRIDAY, JUNE 17TH
	9:30 A.M. -- NOON	8:30 A.M. -- NOON	8:45 A.M. -- NOON	8:30 A.M. -- NOON	8:30 A.M. -- NOON
[illegible]	MA. PLENARY SESSION Donald H. Levy [illegible] D'Cunha Jacques [illegible]		WA. PLENARY SESSION G. Herzberg Ira W. Levin Peter P. Sorokin-- Coblentz Lecturer		
[illegible] LAB		TA. INFRARED (Many Free Radicals)		RA. USSR SPECTROSCOPY (Aliev, Zasavitski, Makushkin, Sinitsa, Krupnov)	FA. INFRARED
[illegible] LAB		TB. ELECTRONIC (Diatomics)		RB. ELECTRONIC (Theory) S. R. Langhoff	FB. ELECTRONIC (Diatomics)
[illegible] LAB		TC. RAMAN(Chlorophyll) TC' PHOTOACOUSTIC		RC. CIRCULAR DICHROISM	FC. MOLECULAR BEAM
[illegible]					FD. RAMAN
			1:30 P.M. -- 5:00 P.M.		
[illegible] LAB	ME. INFRARED ([illegible])	TE. INFRARED D. Papousek	WE. MOSTLY SPHERICAL TOPS	RE. THEORY	
[illegible] LAB	MF. MICROWAVE & [illegible]	TF. ELECTRONIC (Mostly diatomic)	WF. ELECTRONIC (Diatomics)	RF. ELECTRONIC (Mostly triatomics)	
[illegible] LAB	MG. ELECTRONIC ([illegible])	TG. MICROWAVE	WG. RAMAN ([illegible], Carreira, [illegible], [illegible], Barrett)	RG. RAMAN	
[illegible]	MH. VIBRATIONAL ANALYSIS	TH. CONDENSED PHASE (IR & Electronic) TH'	WH. ENERGY TRANSFER WH' MOLECULAR BEAM	RH. MATRIX SPECTRA	

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DATE

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